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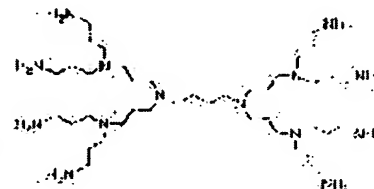
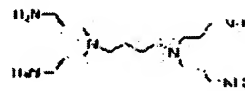
(54) VINYL GROUP-CONTAINING DENDRIMER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a dendrimer enabling the blending ratio of low-molecular compound(s) problematic in safety and/or performance to be lowered by reaction of a specific vinyl group-contg. compound with a specific polyfunctional compound.

SOLUTION: This liquid dendrimer with a number-average molecular weight of pref. 200-100,000 and viscosity (30°C) of pref. 100,000 cps is obtained by reaction of (C) a polyfunctional compound prepared by Michael addition of (B) an active hydrogen-contg. (meth)acrylate-based compound to (A) a polyamino- based

dendrimer with a vinyl group-contg. compound having functional group stoichiometrically equal in amount to the component C and reactive with the active hydrogen in the component C; wherein the component A is e.g. a compound of formula I or formula II. This liquid dendrimer can be directly used as a film-forming material in coating materials or inks, or as an adhesive or the like, as a curable solventless liquid resin, and can also regulate its own viscosity, film formability, etc., through adding a crosslinking agent thereto.



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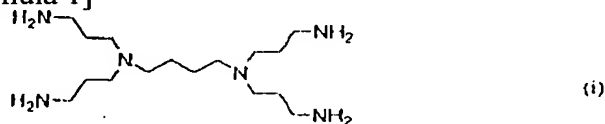
CLAIMS

[Claim(s)]

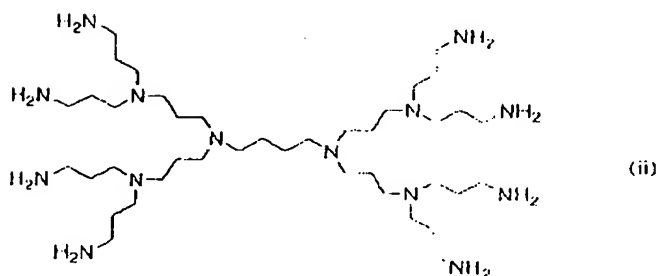
[Claim 1] Vinyl group content DIN DORIMA which comes [stoichiometric] to carry out the amount reaction of the vinyl group content compound (c) which has the functional group in which the active hydrogen with which this multifunctional compound (a) contains an active hydrogen content (meta) acrylate system compound (b) to the multifunctional compound (a) which comes to carry out Michael addition in poly amino system DIN DORIMA and a reaction are possible.

[Claim 2] Vinyl group content DIN DORIMA according to claim 1 whose poly amino system DIN DORIMA is the compound shown by the following type (i) or (ii).

[Formula 1]



4-Cascade: 1,4-Diaminobutane[4] propylamine



8-Cascade: 1,4-Diaminobutane[4];(1-azabutylidene) propylamine

[Claim 3] Vinyl group content DIN DORIMA according to claim 1 active hydrogen and whose vinyl group content compound (c) which has the functional group in which a reaction is possible are isocyanate radical content vinyl compounds (c-1).

[Claim 4] There is no claim 1 whose chain length like the branch which introduced the vinyl group is 9-70 atomic numbers, and it is vinyl group content DIN DORIMA of a publication 3 either.

[Claim 5] There is no claim 1 with below [liquefied] the viscosity of 100000cps (30 degrees C) 200-100000, and number average molecular weight is vinyl group content DIN DORIMA of a publication 4 either.

[Claim 6] There is no claim 1 which is an activity energy-line hardening mold, and it is vinyl group content DIN DORIMA of a publication 5 either.

[Claim 7] There is no claim 1 which is a coating application, and it is vinyl group content DIN DORIMA of a publication 5 either.

[Claim 8] There is no claim 1 which is an ink application, and it is vinyl group content DIN DORIMA of a publication 5 either.

[Claim 9] Claim 1 thru/or the hardened material which comes to irradiate an activity energy line at vinyl group content DIN DORIMA of a publication 8 either.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Industrial Application] This invention relates to vinyl group content DIN DORIMA which can use as resin for objects for coat formation ingredients, such as a coating and ink, or encapsulant, a binder, adhesives, and binders, and can be used as the curing agent or the reactant diluent of heat and a radiation hardening mold resin constituent. Furthermore, this invention relates to vinyl group content DIN DORIMA which can be used as printing ink, the vehicle of a coating, or adhesives as resin of heat or a radiation hardening mold.

[0002]

[Description of the Prior Art] Conventionally, the resin solution containing an organic solvent has been used for a coating, adhesives, a binder, ink, the bulking agent, and the molding material. These resin solutions disperse as a lot of organic solvents at a dry-hard process as [paint and a packer]. With a rise of the interest about earth environment and work environment, the limit to use of such a resin solution is added increasingly. As the one approach, development of resin materials, such as water soluble resin, fine particles, and hot melt, has been furthered. The resin constituent of a drainage system needed the great heating value in order to evaporate the water which is a dispersion medium, and the problem remains also from the point of waste fluid processing, including the organic solvent of the semantics which improves paintwork further to a some in many cases. Moreover, in paint of fine particles or hot melt, and restoration, since the conventional paint and a restoration facility greatly differ from an approach, the need of introducing a new facility is born. In order to solve the above-mentioned problem, high-solid-izing of a resin solution, amelioration of aqueous-ized resin, etc. are performed, and it is thought that the amount of the resin solution used will become still more remarkable [the inclination of a fall] by such efforts from now on. However, as a fundamental solution, there are no problems, such as a public nuisance, insurance health, ignition, and explosion, it can apply broadly and development of coating and the easy non-solvent mold liquefied resin constituent of restoration is demanded strongly.

[0003] A radiation-curing nature resin constituent can be mentioned as a typical thing of a non-solvent mold liquefied resin constituent. The conventional radiation-curing mold resin constituent consists of other resinous principles etc. reactant oligomer, such as hypoviscosity monomers, such as various kinds of acrylate system monomers, and urethane acrylate, epoxy acrylate, or ester acrylate, and also if needed. Although the hypoviscosity monomer was used in order to mainly control the viscosity of a constituent as a reactant diluent, when many this is contained, the volumetric shrinkage at the time of hardening is large, a hardening paint film is brittle, and the odor by the residual monomer in a paint film etc. was made into the problem. Therefore, amelioration of the amount-used mitigation of a reactant diluent, the increment in molecular weight, etc. was desired.

[0004] Moreover, when the flowability of the constituent before hardening was taken into consideration to raise the mechanical engine performance of a hardened material since these materials were the things of hyperviscosity or a solid-state, the reactant diluent of many organic functions, reactant oligomer, and although combination of the amount resin material of macromolecules etc. was still more desirable, combination of a lot of reactant diluents was needed, and there was a limitation in the loadings. Therefore, the hardened material by which the conventional non-solvent mold liquefied resin constituent is being stiffened was a property which is in Haruka in the resin constituent of a solvent system and a drainage system practical deficiently at hardened material properties, such as a degree of hardness, tough nature, a mechanical characteristic, and chemical resistance. Although the radiation-curing mold resin constituent which blended a lot of amount reactivity oligomer of macromolecules and resin materials in order to raise the paint film engine performance is also developed, in order to lower to the viscosity in which coating is possible, a reactant diluent, an organic solvent, etc. of low molecular weight are used, and there is the present condition which is hard to be referred to as that the amelioration on an environment was made.

[0005] Moreover, DIN DORIMA which has a meta-acrylic radical at the end is examined as research of the polymer which has the structure which branched to high orders, such as a tandem type, stellate, and DIN DORIMA, progresses in recent years (Ref. Shi W. et al., J Appl Polym Sci, 59 and 12, 1945(1996)., Moszner N. et al., Macromol chem phys, 197, 2,621(1996). JP,8-231864,A). However, sufficient adhesive property over hardenability or base materials enough as a radiation hardening system material with a well-known compound was not acquired. Moreover, although it can say that it is low viscosity to be sure [as viscosity / the linear compound of the same molecular weight], it blends so much and it cannot be said that the purpose of resin constituent **** of low viscosity is attained enough.

[0006]

[Problem(s) to be Solved by the Invention] This invention offers vinyl group content DIN DORIMA which made it possible to make the rate of combination of the low molecular weight compound which has a problem in safety or an engine-performance side reduce by using the polyfunctional liquefied resin which is hypoviscosity though it is the amount of macromolecules for the purpose of obtaining the non-solvent mold resin constituent which has sufficient paint film engine performance, and was equipped with the low viscosity in which coating is possible. Moreover, this invention can carry out film formation in printing methods, such as the coating approaches used conventionally, such as a roll coater and a knife coating machine, offset printing, gravure, Toppan Printing, and screen-stencil, it can harden by a certain trigger from the former, such as heating, ultraviolet rays, infrared radiation, an electron ray, and gamma irradiation, and vinyl group content DIN DORIMA which can be stiffened without using a catalyst and an initiator especially in the case of an electron ray, gamma irradiation, etc. is offered.

[0007] In order to solve the above-mentioned problem, as a result of inquiring wholeheartedly about the functionality of the structure of various resin systems, and viscosity etc., this invention person found out becoming hypoviscosity and that many end functional groups, such as a vinyl group, could be introduced into 1 molecule from general liner polymer the Kushigata polymer and by changing the molecular structure of many branched polymer and a polymer further, though it was the amount of giant molecules. Furthermore, vinyl group content DIN DORIMA which is new liquefied resin which can be stiffened at high speed was found out by using a certain hardening approach, especially an electron ray as a hardening trigger from the former.

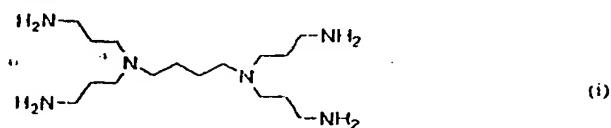
[0008]

[Means for Solving the Problem]

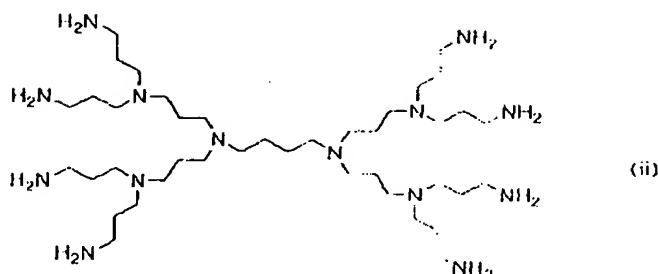
[0009] That is, this invention is a multifunctional compound which makes poly amino system DIN DORIMA come to carry out Michael addition of the active hydrogen content (meta) acrylate system compound (b). Functional group which this multifunctional compound (a) contains to (a) and in which active hydrogen and a reaction are possible Vinyl which comes [stoichiometric] to carry out the amount reaction of the vinyl group content compound (c) which it has It is related with radical content DIN DORIMA. Furthermore, this invention relates to above-mentioned vinyl group content DIN DORIMA whose poly amino system DIN DORIMA is the compound shown by the following type (i) or (ii).

[0010]

[Formula 2]



4-Cascade: 1,4-Diaminobutane[4] propylamine



8-Cascade: 1,4-Diaminobutane[4]:(1-azabutylidene)-4-propylamine

[0011] Furthermore, this invention relates to above-mentioned vinyl group content DIN DORIMA active hydrogen and whose vinyl group content compound (c) which has the functional group in which a reaction is possible are isocyanate radical content vinyl compounds (c-1). Furthermore, this invention relates to above-mentioned vinyl group content DIN DORIMA whose chain length like the branch which introduced the vinyl group is 9-70 atomic numbers. Furthermore, number average molecular weight is 200-100000, and this invention relates to above-mentioned vinyl group content DIN DORIMA with below [liquefied] the viscosity of 100000cps (30 degrees C). Furthermore, this invention relates to above-mentioned vinyl group content DIN DORIMA which is an activity energy-line hardening mold. Furthermore, this invention relates to above-mentioned vinyl group content DIN DORIMA which is a coating application.

[0012] Furthermore, this invention relates to above-mentioned vinyl group content DIN DORIMA which is an ink application. Furthermore, this invention relates to the hardened material which comes to irradiate an activity energy line at above-mentioned vinyl group content DIN DORIMA.

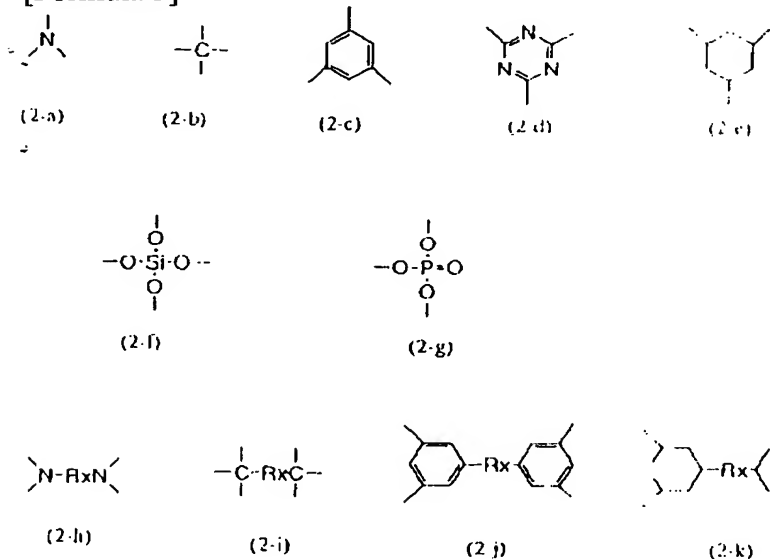
[0013] Generally vocabulary called DIN DORIMA has been used to the high multi-branching compound of the regularity which branched to altitude. However, it is the present condition out of which various multi-branching compounds with the low regularity aiming at simplifications of a synthesis method, such as development of the dendritic compound by the 1 step method etc., are developed as new DIN DORIMA, and a conclusion has not yet come about the nomenclature with advance of the research on the synthesis method of the latest DIN DORIMA. Then, in this invention, DIN DORIMA shall mean the multi-branching compound which branched in three dimensions, and high DIN DORIMA of the low hyper-branch (hyper-branched) of regularity and regularity shall be named generically. As this DIN DORIMA was shown in drawing 1, at least a core part and a branch consist of about a tee and end grade. The number about the number of the branches further combined with the model Fig. of DIN DORIMA of the smallest unit in this invention and standard DIN DORIMA and the core part which each DIN DORIMA contains, the number like a branch, and a tee, and like an end is shown in drawing 1.

[0014] In this invention, a core part and a tee are the structures which at least three branches combined, for example, the following formula (2-a) and (2-b) can be mentioned as what consists of one atoms, and what is shown as what consists of ring compounds by the following formula (2-c), (2-d), and (2-e) is mentioned. Moreover, it supposes that a structure metallurgy group atom as shown by the formula (2-f) is also at least as a core part or a tee, and can illustrate (2-g). In addition, the structure shown by following general formula (2-h) - (2-k) is the core section. It is instantiation of the structure equivalent to seeing of an about, and the core parts of this structure are four or more branches. It can have and is desirable. Moreover, the distinction a core part and like a tee is the DIN DORIMA **. It shall be set from the structure of the start raw material at the time of **. the inside Rx of the following structure expression -- carbon number 1-12 -- it is the alkylene group of 1-6

preferably.

[0015]

[Formula 3]



[0016] Although it is the generic name of the configuration part where at least one core part or a tee, and an adjoining tee combine an end at least in a branch and especially structure is not limited in this invention, it shall consist of at least four atoms. Moreover, at least five numbers [7-125] like the branch which exists in DIN DORIMA 1 molecule are 9-100 pieces still more preferably preferably. Moreover, in this invention, the end which vinyl group content DIN DORIMA contains is the vinyl group fundamentally shown by formula (8-1) - (8-7).

[0017] Moreover, generally the magnitude is expressed with conceptual vocabulary called a generation (generation) the right DIN DORIMA case of regularity. In this invention, the branching structure which left the core compound of the above-mentioned definition is called 1st generation DIN DORIMA, and the structure which has the branching structure which branched from all the end grades of the 1st generation is called second generation. Third generation DIN DORIMA which has at least the core part which four branches combined with drawing 2, and an end was shown, and each generation was further shown all over drawing. This is considered as the definition of a generation in this invention.

[0018] Moreover, in this invention, the active hydrogen content end functional group which a multifunctional compound (a) has is a reactive site for introducing a vinyl group. In this invention, a multifunctional compound (a) contains preferably five or more active hydrogen [6-128] which contains preferably at least three four - active hydrogen content end functional groups [64], and originates in 1 molecule at it. The organic residue which contains the active hydrogen shown below, for example as the above-mentioned active hydrogen content end functional group can be mentioned.

- NH_2 : First-class amino group (3-1)

- NHR_1 : The second class amino group (R_1 is the alkyl group of carbon numbers 1-3) (3-2)

- COOH : Carboxyl group (3-3)

- OH : Hydroxyl group (3-4)

- $\text{Si}(\text{OR})_3\text{-n}(\text{OH})_n$ (integer of $n=1-3$)

; Hydroxy silyl radical (3-5) - $\text{P}=\text{O}_2(\text{OH})$: Phosphoric-acid radical (3-6)

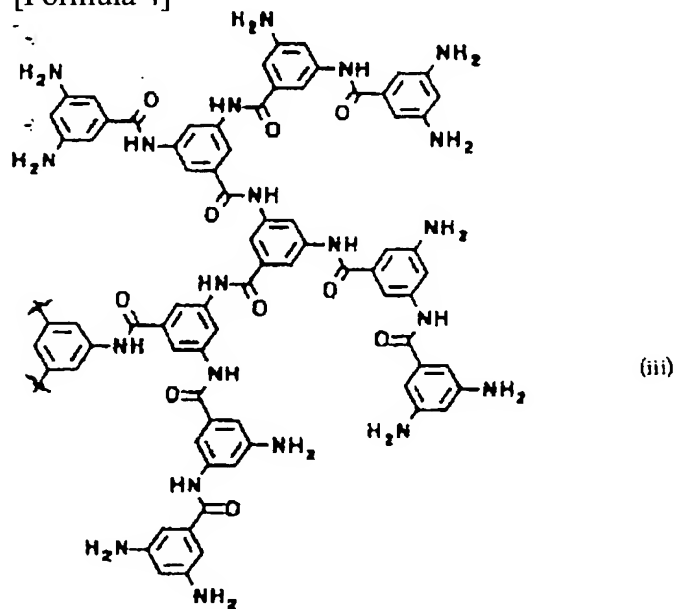
Although especially the class of active hydrogen content end functional group is not limited, it is chosen from affecting paint film physical properties according to the structure of a bond part according to the physical properties fundamentally made into the purpose. If the first-class amino group, a hydroxy silyl radical, and a phosphoric-acid radical are used, more vinyl groups can be introduced.

[0019] moreover, as poly amino system DIN DORIMA which has an amino group at the end in this invention The butylene diamine and acrylonitrile which were shown by the above-mentioned formula (i) and (ii) are made to react. Propyleneimine system DIN DORIMA obtained by using as one step the reaction which returns the nitrile group of an end to an amine, and repeating this reaction (WO 093/14147, US5530092, JP,7-330631,B), Michael addition of the methyl acrylate is carried out at ammonia or ethylenediamine. Furthermore, the reaction which introduces the second class amino group into an end by ester transamidation is used as one step. Amide amine system DIN DORIMA (WO 84/02705, JP,6-70132,B) shown with the following structure

expression (iv) obtained by making it react repeatedly if needed, or its intermediate product, Moreover, the compound of the following formula (i ii) and the structure shown by (v) etc. can be mentioned.

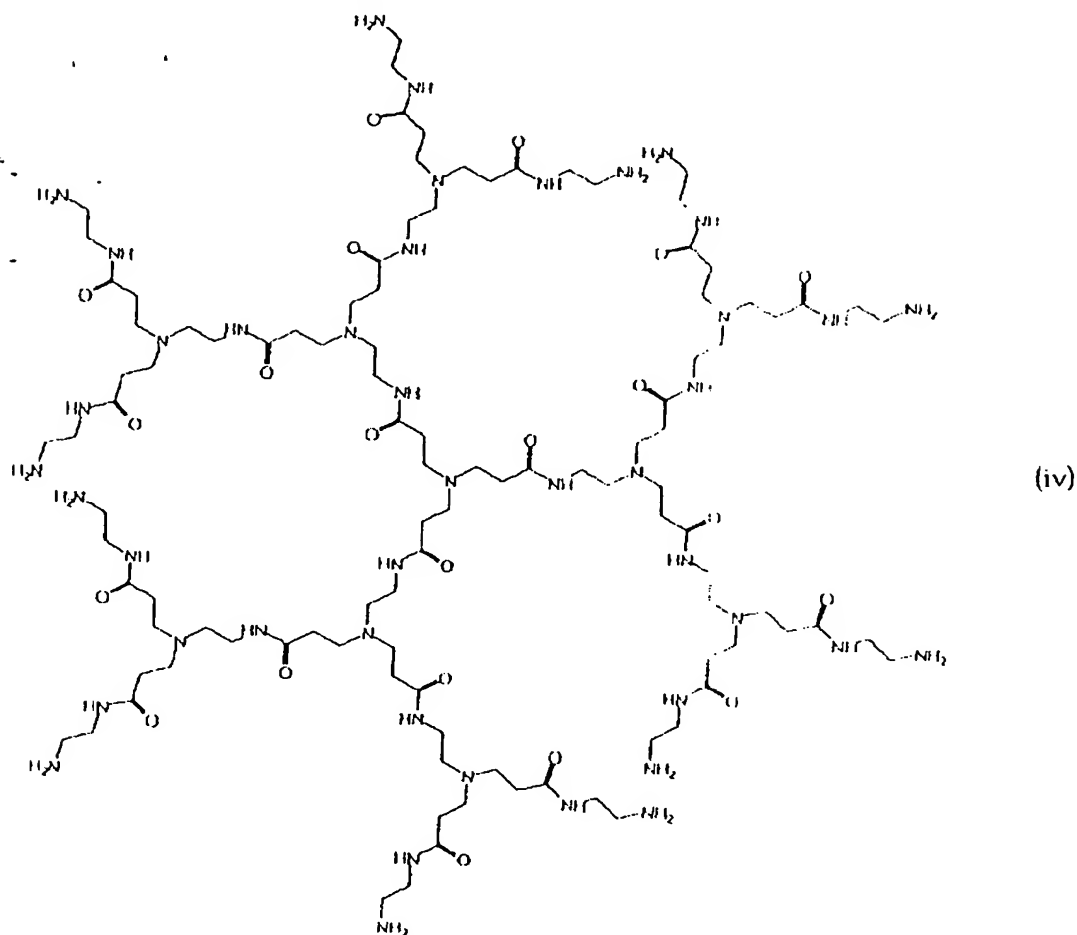
[0020]

[Formula 4]



[0021]

[Formula 5]

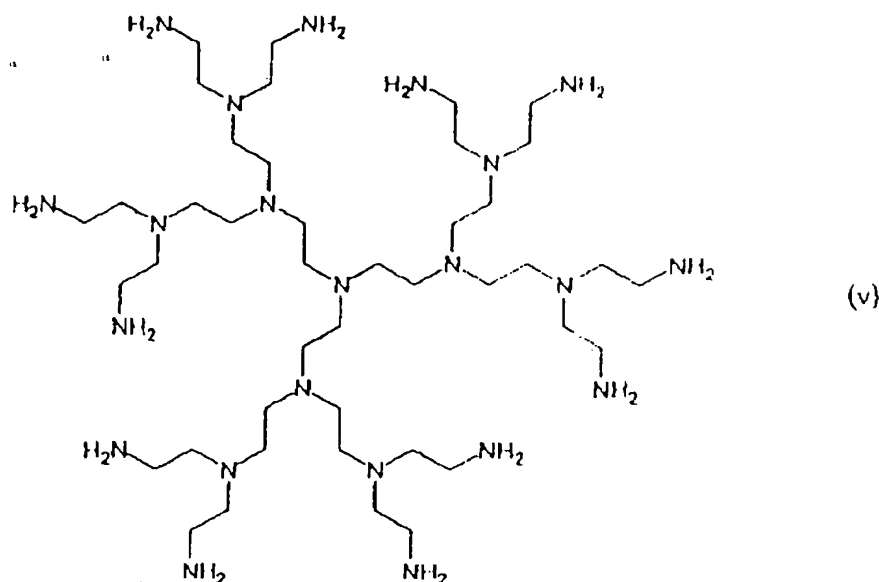


12-Cascade:ammonia[3]:

(1,4-diaza-5-oxoheptylidene)²:3-aza-4-oxohexylamine

[0022]

[Formula 6]



12-Cascade:ammonia[3]:(1-azapropylidene)²:ethylamine

[0023] Although especially the desirable magnitude of high DIN DORIMA of the regularity used in this invention is not limited, 1-5 generations of 1-3 generations of things having the desirable viscosity before hardening and the physical properties after hardening will be preferably obtained, if 1 or DIN DORIMA of two generations is used still more preferably especially. Poly amino system DIN DORIMA shown as this DIN DORIMA of one generation or two generations by the above-mentioned formula (i) currently produced commercially from the DSM company or (ii) is desirable from the point of the ease of receiving.

[0024] Moreover, in this invention, although especially the number average molecular weight of the multifunctional compound (a) used is not limited, it may be dealt with as number average molecular weight as desirable molecular weight range from 30-50000, and it being the compound of 50-5000 still more preferably, and viscosity becoming high or number average molecular weight being a solid-state, when it is 50000 especially or more, 5000 and, and may not be desirable a top.

[0025] In this invention, the multifunctional compound (a) used is obtained by carrying out Michael addition of poly amino system DIN DORIMA which has the amino group of the first class or the second class, and the active hydrogen content (meta) acrylate system compound (b). Vinyl group content DIN DORIMA which has the desirable viscosity before hardening and a hardened material property can be obtained.

[0026] The above-mentioned active hydrogen content (meta) acrylic compound (b) Hydroxyalkyl (meta) acrylate system compound which is an acrylic compound which has one or more hydroxyl groups, a carboxyl group, etc. in a molecule (meta), for example, is shown by the following formula (4) CH₂=C(R1) COO-R2-OH (the alkyl group of 2-16 is expressed preferably, respectively. the inside of a formula, and R1 -- a hydrogen atom, or CH₃ and R2 -- carbon numbers 2-22 --) (4)

Polyalkylene glycol monochrome (meta) acrylate system compound shown by the following formula (5) CH₂=C(R1) COO(C_xH_{2x}O) mH (5)

(the inside of a formula, and R1 -- a hydrogen atom or CH₃ and x -- 1-6 -- desirable -- the integer of 2-4, and m -- 1-25 -- the integer of 4-16 is expressed preferably, respectively.)

The poly lactone monochrome (meta) acrylate system compound shown by the following formula (6), CH₂=C(R1) COOCyH_{2y}O(COCzH_{2z}O) kH (6)

(the inside of a formula, and R1 -- a hydrogen atom, or CH₃ and y -- 2-22 -- desirable -- the integer of 2-16, and z -- 2-15 -- desirable -- the integer of 3-5, and k -- 1-20 -- the integer of 1-5 is expressed preferably, respectively.)

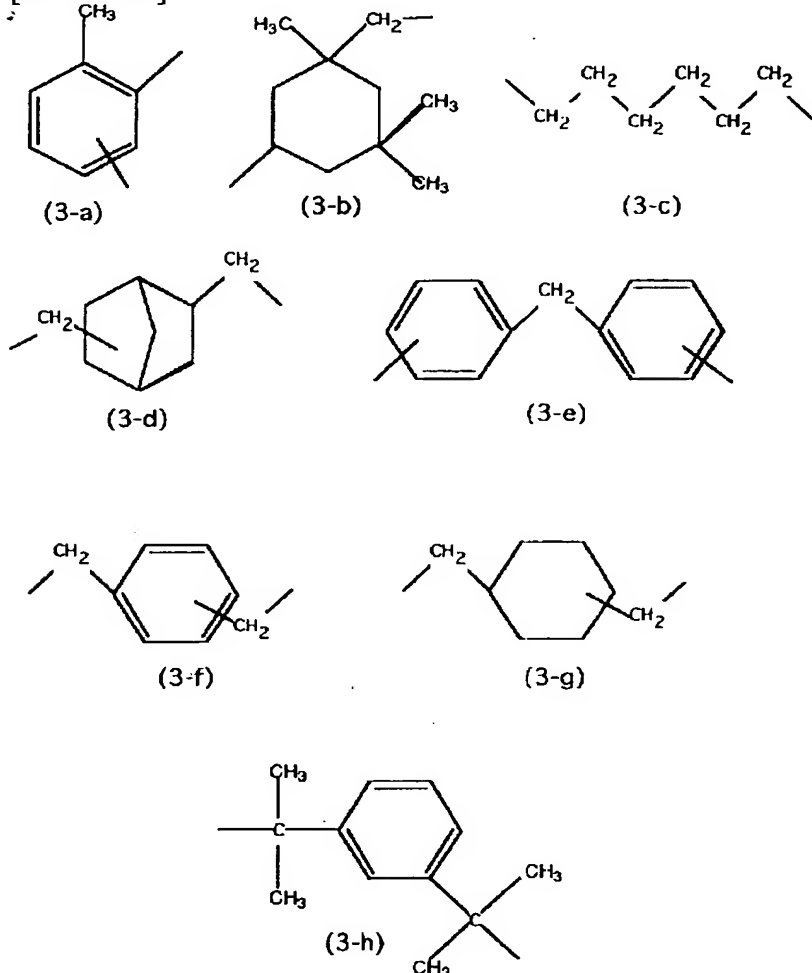
Or it is the urethane monochrome (meta) acrylate system compound shown by the following formula (7).

[0027]

CH₂=C(R₁) COR₃O [CONHR₄NHOR₅O] hH (7) (the inside of a formula, and R₁ -- a hydrogen atom, or CH₃ and R₃ -- the alkyl group of carbon numbers 2-22 --) among the isocyanate residue R₄ is indicated to be by following type (3-a) - (3-h), the dihydric alcohol residue R₅ is indicated to be by -(CpH₂pO) q- or -CpH₂p-, and a formula, the integer of 1-4 and q express the integer of 1-100, and, as for h, p expresses the integer of 1-10, respectively.

[0028]

[Formula 7]



[0029] what has chain length short when a hard hardened material is needed in this invention as chain length of the above-mentioned active hydrogen content (meta) acrylic compound (b) -- moreover, chain length's long thing is desirable in order to raise flexibility. In above-mentioned within the limits, although molecular weight increases with extension of chain length, the inclination for bulk viscosity to fall is shown. In being longer than the above-mentioned range, the bulk viscosity of vinyl group content DIN DORIMA becomes high, or in ordinary temperature, it is a solid-state, hardenability becomes scarce further, and, for a certain reason, things are also desirable. It is and is **.

[0030] Furthermore, when an example is given, as a hydroxyalkyl (meta) acrylate system compound shown in the general formula (4), there are 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 4-hydroxy butyl (meta) acrylate, 2-hydroxy butyl (meta) acrylate, etc.

[0031] As an alkylene glycol monochrome (meta) acrylate system compound shown by the general formula (5), there are diethylene-glycol monochrome (meta) acrylate, TORIECHIREN grumble call monochrome (meta) acrylate, tetraethylene glycol monochrome (meta) acrylate, dipropylene glycol monochrome (meta) acrylate, tripropylene glycol monochrome (meta) acrylate, tetrapropylene glycol monochrome (meta) acrylate, polytetramethylene glycol monochrome (meta) acrylate, etc., for example.

[0032] As a poly lactone monochrome (meta) acrylate system compound shown by the general formula (6), there are 2-(meta) acryloyloxyethyl hydrogen KAPURORAKUTONETO, 2-(meta) acryloyloxyethyl hydrogen JIKAPURORAKUTONETO, 2-(meta) acryloyloxyethyl hydrogen poly (degrees of polymerization 3-5) KAPURORAKUTONETO, 2-(meta) acryloyloxyethyl-2-hydroxy-6 hexano RAKUTONETO, etc.

[0033] Also besides having been shown in above-mentioned general formula (4) - (7), furthermore, 2-(meta)

acryloyloxyethyl 2-hydroxypropyl phthalate, There are 3-chloro-2-hydroxypropyl (meta) acrylate and 2-hydroxy-3-phenoxy propyl (meta) acrylate. Moreover, glycerol monochrome (meta) acrylate, pentaerythritol monochrome (meta) acrylate, Ethyleneoxide denaturation pentaerythritol monochrome (meta) acrylate, trimethylol propane monochrome (meta) acrylate, ethyleneoxide denaturation trimethylol propane monochrome (meta) acrylate, etc. can be used.

[0034] Moreover, as an acrylic compound which has a carboxyl group (meta), a maleic acid, a fumaric acid, an itaconic acid, citraconic acids, such alkyls or alkenyl monoester, phthalic-acid beta-(meta) acryloxyethyl monoester, isophthalic acid beta-(meta) acryloxyethyl monoester, terephthalic-acid beta-(meta) acryloxyethyl monoester, succinic-acid beta-(meta) acryloxyethyl monoester, an acrylic acid, a methacrylic acid, etc. can be used into a molecule.

[0035] Although it will not be restricted especially if at least one active hydrogen content (meta) acrylic compound (b) is added as loadings of the above and an active hydrogen content acrylic compound (b) in this invention, it is 50% or more still more preferably 10% or more preferably to all the active hydrogen of the poly amino system DIN DORIMA origin. Since multi-branching structure is hard to be acquired and the description of the (b) component is sufficiently hard to be reflected when fewer than this, it may not be desirable.

[0036] Although the above and the synthetic approach of a multifunctional compound (a) can be performed according to a conventional method, if alcohol, such as a methanol and ethanol, is used as a reaction solvent, side reaction cannot occur easily. In case a solvent is used, it is desirable to use it one to 100 times to the combination weight of poly amino system DIN DORIMA. Moreover, although especially heating is not needed, when the molecular weight of poly amino system DIN DORIMA or (meta) an acrylic compound is large, it is desirable to heat in 30 degrees C - 70 degrees C. Reaction time is 1 - 10 hours, when it generally warms at extent and 50-100 degrees C in ordinary temperature with the class and reaction temperature of the amino compound to be used one whole day and night for 30 minutes to 72 hours, although it is various. Less than, it ends.

[0037] Although it will not limit especially if it is introduced in order that a vinyl group may give reactivity to a multifunctional compound (a) in this invention, and it has the double bond of polymerization nature, desirable structure is shown below.

CH₂=CHCOO - ; Acrylic radical (8-1)

CH₂=CH(CH₃) COO-; meta-acrylic radical (8-2) CH₂=CH - ; Vinyl group (8-3)

CH₂=CH-CH₂-O - ; Allyl group (8-4) -CH=CH - ; Dienyl radical (8-5)

CH₂=CH-C₆H₄ - ; Phenyl vinyl group (8-6)

CH₂=CH-O - ; Vinyl ether radical (8-7)

Among the above-mentioned vinyl groups, by the reactant point at the time of radiation hardening to UV hardening, an acrylic radical is desirable, comparatively high hardenability is shown by the methacrylic radical at the time of electron ray hardening, and it can be said from both sides of reactivity and safety that it is desirable. Moreover, the concomitant use with an acrylic radical and a vinyl ether radical is desirable from the field of the improvement in hardenability.

[0038] Moreover, with the chain length like the branch which introduced the vinyl group in this invention, it considers as the atomic number which counted from the degree of the joint atom like the tee which the end vinyl group combined, and was combined with linear one to the first X-CH=CH-(X is hydrogen atom or organic residue) structure. When it contains ring structures, such as a ring, a cyclo ring, and heterocycle, on the way, the number of association with a ring structure will be replaced with an atomic number, and will be counted. the desirable chain length like the branch which took to this invention and introduced the vinyl group - 2-100 -- it is 9-70 still more preferably.

[0039] In this invention, vinyl group content DIN DORIMA is obtained by introducing a vinyl group into the above-mentioned multifunctional compound (a), and, fundamentally, is obtained by the reaction with the vinyl group content compound (c) which has the active hydrogen content end functional group which a multifunctional compound (a) contains, and the functional group in which active hydrogen and a reaction are possible. Although the functional group in which active hydrogen and a reaction are possible is chosen by the class of active hydrogen content end functional group which a multifunctional compound (a) contains in this invention for example, when the active hydrogen content end functional group which a multifunctional compound (a) has is the first class or the second class amino group An acrylic radical, a carboxyl group, a hydroxyl group, and an epoxy group are desirable. Again When an active hydrogen content end functional group is a hydroxyl group, an isocyanate radical, an epoxy group, an alkoxy silyl radical, a phosphoric-acid radical, or a carboxyl group is desirable, and an epoxy group is desirable when an active hydrogen content end functional group is a carboxyl group further. Although the active hydrogen which can be used when the end of a multifunctional compound (a) is an amino group, and the compound which has acryloyl radicals, such as 2-

hydroxy-3-acryloxypropyl methacrylate, and other vinyl groups as a vinyl group content compound (c) which has the functional group in which a reaction is possible can be illustrated, since an acrylic radical cannot be introduced into an end in this case, hardenability sufficient especially as an ultraviolet-rays hardenability compound may be hard to be acquired.

[0040] As a vinyl group content compound (c) which has the functional group which can be used when the above-mentioned end is a hydroxyl group, and in which active hydrogen and a reaction are possible For example, glycidyl (meta) acrylate, 3, 4-epoxycyclohexyl (meta) acrylate, 1-vinyl -3, 4-epoxy cyclohexane, acrylate (meta (3, 4-epoxycyclohexyl-5-hydroxy hexano IKKU carboxylate)), Epoxycyclohexyl methyl poly caprolactone (meta) acrylate, End epoxy system vinyl group content compound compounds, such as allyl glycidyl ether and vinyl cyclohexyl epoxide, Vinyltrimetoxysilane, vinyltriethoxysilane, 3-methacryloxy propyl trimethoxysilane, End alkoxy silyl system vinyl group content compounds, such as gamma-methacryloxypropyl dimethoxysilane, Phospho [acid phosphoxyethyl methacrylate and 3-chloro-2-acid] KISHIPURO pill methacrylate, Acid HOSUHOKISHI propyl methacrylate, acid phosphoxyethyl methacrylate, End phosphoric-acid system content vinyl group content compounds, such as acid HOSUHOKISHI polyoxy-ethylene-glycol mono-methacrylate and ASHIDDOHOSUHOKISHI polyoxypropylene glycol mono-methacrylate, etc. can be mentioned.

[0041] Moreover, since it goes on under conditions especially with a mild combination of a hydroxyl group and an isocyanate radical, if the active hydrogen content end functional group which a multifunctional compound (a) has when the isocyanate radical content vinyl compound (c-1) which has an isocyanate radical is used can use it in the case of a hydroxyl group, a carboxyl group, the amino group, etc., and the stability of the vinyl group of an end is taken into consideration, it can be said that it is desirable.

[0042] Desirable use about the above-mentioned isocyanate radical content vinyl compound (c-1) As an approach, a vinyl group can be introduced into poly amino system DIN DORIMA, for example by carrying out the addition reaction of the isocyanate radical content vinyl compound (c-1) to the multifunctional compound (a) obtained by carrying out Michael addition of the active hydrogen content (meta) acrylate system compound (a-1).

[0043] As the above-mentioned isocyanate radical content vinyl compound (c-1), they are methacryloiloxy-ethyl isocyanate (MOI), vinyl isocyanate, allyl compound isocyanate, acryloyl (meta) isocyanate (MAI), and isopropenyl, for example. - There is alpha and alpha-dimethylbenzyl isocyanate (TMI) etc. Moreover, in this invention, the compound to which the vinyl compound (c-3) containing a diisocyanate compound (c-2), an isocyanate radical, and the functional group in which a reaction is possible was made to react by equimolar can also be used as an isocyanate radical content vinyl compound (c-1).

[0044] As the above-mentioned diisocyanate compound (c-2) 1, 6-G SOSHIANATO hexane, a JIISO cyanic-acid isophorone, the JIISO cyanic acid 4, 4'-diphenylmethane, Polymeric diphenylmethane diisocyanate, xylylene diisocyanate, JIISO cyanic-acid torr toluylene, JIISO cyanic-acid hexamethylene, JIISO cyanic-acid 4-methyl-m-phenylene, Naphthylene diisocyanate, PARAFENI range isocyanate, tetramethyl xylylene diisocyanate, Cyclo hexylmethane diisocyanate, hydrogenation xylylene diisocyanate, Cyclohexyl diisocyanate, 2 and 2, 4-trimethyl hexamethylene di-isocyanate, 2, 4, and 4-trimethyl hexamethylene di-isocyanate, m-tetramethyl xylylene diisocyanate, p-tetramethyl xylylene diisocyanate, dimer acid diisocyanate, etc. can be mentioned.

[0045] Moreover, although the vinyl compound which has the amino group, a hydroxyl group, a carboxyl group, etc. as a vinyl compound (c-3) containing the isocyanate radical and the functional group in which a reaction is possible which are used in this invention is mentioned, what has a hydroxyl group and a carboxyl group is desirable from a reactant field with an isocyanate radical. Although what contains only one hydroxyl group among the above-mentioned compounds can be used as an acrylic compound which has this hydroxyl group (meta), and molecular weight is comparatively low, the direction is desirable from a reactant field with diisocyanate, for example, can mention 4-hydroxy butyl (meta) acrylate, 2-hydroxyethyl (meta) acrylate, 2-(meta) acryloyloxyethyl hydrogen KAPURORAKUTONETO, etc.

[0046] In this invention, amount combination of the active hydrogen and active hydrogen which a multifunctional compound (a) contains, and the vinyl group content compound (c) which has the functional group in which a reaction is possible can be carried out [stoichiometric], and vinyl group content DIN DORIMA can be obtained by making it react. For example, the active hydrogen content functional group which a multifunctional compound (a) has is a hydroxyl group, and when introducing a vinyl group into an end with an isocyanate radical content vinyl compound (c-1), the synthetic approach can be performed according to a conventional method. Although a non-solvent system is also compoundable, if ethyl acetate, a methyl ethyl ketone, etc. are used as a reaction solvent if needed, since temperature control is easy, side reaction cannot occur easily. In case a solvent is used, it is desirable that NV of the system of reaction makes it to 20 - 90%.

Moreover, the catalyst of tin systems, such as the catalyst used if needed at the time of the usual urethane composition, for example, octylic acid tin, and 2-ethylhexanoic acid tin, etc. may be added. The addition of a desirable catalyst receives an isocyanate radical content vinyl compound (c-1), and is 1 - 0.01 % of the weight. It is desirable to heat in 30 degrees C - 70 degrees C as reaction temperature. With the dilution ratio by the solvent, the amount of catalysts, reaction temperature, etc., although reaction time is various, it is ended in 30 minutes - about 72 hours.

[0047] moreover, vinyl group content DIN DORIMA obtained by this invention -- number average molecular weight 200-100000 -- desirable -- 300-50000 -- it is 400-40000 still more preferably, and 100000cps or less of 50000-500cps of 20000-1000cps viscosity (30 degrees C) is shown still more preferably preferably -- it is liquefied. Since hardening contraction will become intense if molecular weight is lower than this, it is not desirable. Moreover, especially when it is the viscosity range in which film formation is possible as viscosity, it is not a problem, but if the above-mentioned range is crossed, it is not desirable in respect of solubility with that the loadings of low molecular weight compounds, such as that the handling of combination etc. is inconvenient and a reactant diluent, increase, and other components etc.

[0048] Although vinyl group content DIN DORIMA obtained in this invention can be used as coat formation ingredients, such as a coating and ink, a molding material, adhesives, etc. as non-solvent liquefied resin of hardenability even if it remains as it is, by mixing addition for cross linking agents, such as an acrylic (meta) compound of monofunctional or many organic functions, the poly isocyanate, and a melamine, it can adjust viscosity or can adjust film formation nature and the coat engine performance. Moreover, since it is the same, even if it blends curing agent resin, such as amino resin and phenol resin, it does not interfere. Moreover, in order to raise the coat engine performance, drying oil, such as the reactant resin and the linseed oil which have vinyl groups, such as general-purpose polymers, such as well-known polyamide resin, a cellulosic, vinyl system resin, polyolefine, a natural rubber derivative, acrylic resin, an epoxy resin, polyester, and polystyrene, urethane acrylic resin, epoxy acrylic resin, ester acrylic resin, an alkyd resin, a rosin denaturation alkyd resin, and a linseed-oil denaturation alkyd resin, tung oil, and soybean oil, etc. may be blended. However, each of these loadings is 20 or less % of the weight still more preferably 40% of the weight preferably. Furthermore, water or an organic solvent, a compatibilizer, a surfactant, or lubricant may be added if needed. These loadings are 10 or less % of the weight still more preferably 20% of the weight preferably.

[0049] It can be used as various printing ink, a coloring coating, etc. by carrying out suitable amount addition of the inorganic bulking agents, such as a coloring agent which becomes vinyl group content DIN DORIMA obtained by this invention from pigments, such as a color, carbon black, a titanium white, a phthalocyanine, azo dye, and Quinacridone, Si system particle and a mica, and a calcium carbonate, etc. Moreover, when you make it harden by the exposure of an activity energy line, a well-known photopolymerization sensitizer and a well-known initiator can be added.

[0050] vinyl group content DIN DORIMA of this invention -- a plates [, such as various metals, plastics, and paper,], film, and sheet top -- a roll coater, bar coater, knife coater, etc. -- coating -- or it can be filled up and you can make it harden under -5-300-degree C temperature conditions Moreover, constituents for coat formation ingredients using vinyl group content DIN DORIMA of this invention, such as ink and a coating Metal plates, such as various steel plates and an aluminum plate, plastic film, paper, To base materials, such as a plastic film laminated paper, by a certain approach from the former, such as printing methods, such as the coating approaches, such as a roll coater and a knife coating machine, or offset printing, gravure, Toppan Printing, and silk screen printing You can carry out film formation in 0.1-500-micrometer thickness, and can make it harden by irradiating activity energy lines, such as heating or an electron ray, ultraviolet rays, a visible ray, and infrared radiation.

[0051] When you make it harden by electron beam irradiation, 10-1000kV of electron-beam-irradiation equipment which has the acceleration voltage of the range of 30-300kV still more preferably is used preferably. The electron-beam-irradiation equipment of low acceleration voltage is more effective for hardening of a thin film, in order that energy may concentrate on a front face, and the damage to a paint film or a base material is desirable from few things. The range of the acceleration voltage in this case is 30-70kV. Moreover, the quantity of radiation (DOSE) of an electron ray is the range of 5-200kGy still more preferably one to 1000 kGy preferably. Since the damage to a paint film or a base material is serious when larger [if fewer than this, enough hardened materials will be hard to be obtained, and] than this, it is not desirable.

[0052]

[Example] Next, although an example explains this invention to a detail further, this invention is not limited to this.

O the measuring method of structural analysis, number average molecular weight, and viscosity -- the structure of vinyl group content DIN DORIMA compounded 1 structural analysis here was checked by 1 H-NMR.

2) Number average molecular weight : gel permeation chromatography (TOSOH SC-8020)

The calibration curve of a gel par MESHON chromatograph (GPC) was uniquely created from some kinds of vinyl group content DIN DORIMA of structure known analyzed by $^1\text{H-NMR}$, and the result measured by GPC based on this was adopted. Moreover, the value acquired in this measuring equipment was used for molecular weight distribution (M_w/M_n).

3) Viscosity : rheometer (LEO metrics company make: RDS-II, RFS-II)

The stationary viscosity (ZURI rate = value of 10 [1-]/sec) measured in accordance with the viscosity of a sample by rheometer RDS-II (hyperviscous type) by the LEO metrics company or RFS-II (hypoviscosity type) was adopted, respectively.

O Electron-beam-irradiation equipment and exposure condition 1 area beam type electron-beam-irradiation equipment Curetron EBC-200-20-30 (the Nissin high voltage)

Electron-ray acceleration: 200kVDOSE was adjusted with the amount of currents in the range of 5-80kGy.

2) MIN-EB (AIT company make)

Electron ray acceleration: 60kVDOSE was adjusted at the band-conveyor rate in the range of 5-80kGy.

[0053] O Describe the cable address of the compound of the following used in the example and the example of a comparison.

1) Multifunctional-compound DAB4:8-Cascade;1, 4-Diaminobutane[4];propylamineDAB8:16-Cascade;1, a 4-Diaminobutane[8];propylamine2 active-hydrogen content (meta) acrylic compound (b)

4HBA:4 - hydroxy butyl acrylate HEA:2-hydroxyethyl acrylate PPG6A:polypropylene-glycol (degree of polymerization of PPG chain = 6) acrylate PEG7A -- :polyethylene-glycol (degree of polymerization of PEG chain = 7) acrylate PCL2A:2-(meta) acryloyloxyethyl hydrogen JIKAPURORAKUTONETO (plaque cel FAmade from Die Cel Chemistry- 2)

SA: 2-acryloyloxyethyl ethyl hydrogen succinate 3 isocyanate radical content vinyl compound (c-1)

MOI: Methacryloiloxy-ethyl isocyanate TMI: Synthetic compounds shown in dimethyl meta-ISOPIROPE nil benzyl isocyanate and the examples 1-6 of the following composition [0054] The equimolar adduct churning equipment of tolylene diisocyanate (TDI) and 4HBA(s), (Synthetic example 1) Nitrogen installation tubing, a thermo sensor, a capacitor, and 4HBA:144g, To the 1000ml 4 opening round bottom flask equipped with the dropping funnel filled up with the mixed solution of 144g of ethyl acetate, TDI:174g, Ethyl acetate: It is ** with the water bath which blended 174g and 2-ethylhexanoic acid tin:0.2g, and was set as 50 degrees C. The above-mentioned solution with which it was filled up into the dropping funnel was dropped in 1 hour, carrying out heat churning. The reaction was ended in the place where NCO ** became below a theoretical value with the titrimetric method.

[0055] The equimolar adduct churning equipment of isophorone diisocyanate (IPDA) and 4HBA(s), (Synthetic example 2) Nitrogen installation tubing, a thermo sensor, a capacitor, and 4HBA:144g, To the 1000ml 4 opening round bottom flask equipped with the dropping funnel filled up with the mixed solution of 144g of ethyl acetate, IPDI:222g, Ethyl acetate: 220g and 2-ethylhexanoic acid tin:0.2g were blended, and the above-mentioned solution with which it was filled up into the dropping funnel was dropped in 1 hour, carrying out heating churning with the water bath set as 50 degrees C. The reaction was ended in the place where NCO ** became below a theoretical value with the titrimetric method.

[0056] The equimolar adduct churning equipment of TDI and HEA, nitrogen installation tubing, (Synthetic example 3) To the 1000ml 4 opening round bottom flask equipped with the dropping funnel filled up with a thermo sensor, a capacitor and HEA:116g, and the mixed solution of 120g of ethyl acetate, TDI:174g, Ethyl acetate: 174g and 2-ethylhexanoic acid tin:0.2g were blended, and the above-mentioned solution with which it was filled up into the dropping funnel was dropped in 1 hour, carrying out heating churning with the water bath set as 50 degrees C. The reaction was ended in the place where NCO ** became below a theoretical value with the titrimetric method.

[0057] The equimolar adduct churning equipment of IPDI and HEA, nitrogen installation tubing, (Synthetic example 4) To the 1000ml 4 opening round bottom flask equipped with the dropping funnel filled up with a thermo sensor, a capacitor and HEA:116g, and the mixed solution of 120g of ethyl acetate, IPDI:222g, Ethyl acetate: 220g and 2-ethylhexanoic acid tin:0.2g were blended, and the above-mentioned solution with which it was filled up into the dropping funnel was dropped in 1 hour, carrying out heating churning with the water bath set as 50 degrees C. The reaction was ended in the place where NCO ** became below a theoretical value with the titrimetric method.

[0058] The equimolar adduct churning equipment of hexamethylene di-isocyanate (HMDI) and HEA, (Synthetic example 5) Nitrogen installation tubing, a thermo sensor, a capacitor, and HEA:116g, To the 1000ml 4 opening round bottom flask equipped with the dropping funnel filled up with the mixed solution of 120g of ethyl acetate, HMDI:168g, Ethyl acetate: 170g and 2-ethylhexanoic acid tin:0.2g were blended, and the above-

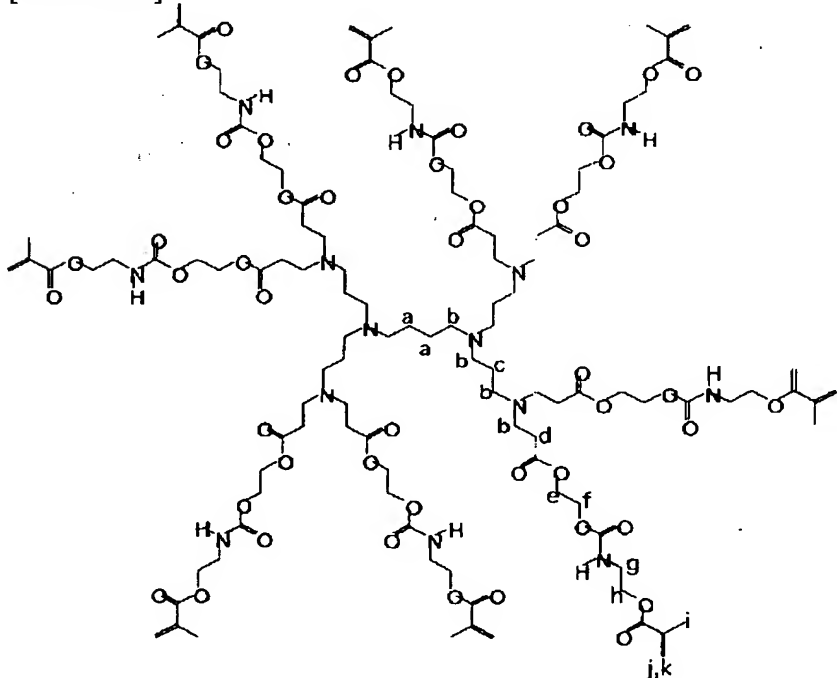
mentioned solution with which it was filled up into the dropping funnel was dropped in 1 hour, carrying out heating churning with the water bath set as 50 degrees C. The reaction was ended in the place where NCO ** became below a theoretical value with the titrimetric method.

[0059] The equimolar adduct churning equipment of HMID and 4HBA(s), nitrogen installation tubing, (Synthetic example 6) To the 1000ml 4 opening round bottom flask equipped with the dropping funnel filled up with a thermo sensor, a capacitor and 4HBA:144g, and the mixed solution of 140g of ethyl acetate, HMDI:168g, Ethyl acetate: 170g and 2-ethylhexanoic acid tin:0.2g were blended, and the above-mentioned solution with which it was filled up into the dropping funnel was dropped in 1 hour, carrying out heating churning with the water bath set as 50 degrees C. The reaction was ended in the place where NCO ** became below a theoretical value with the titrimetric method.

[0060] (Example 1) 4:31.6 g DAB, HEA:92.8g, and ethyl-acetate:125g were blended with the 1000ml 4 opening round bottom flask equipped with churning equipment, nitrogen installation tubing, the thermo sensor, and the capacitor, and after making it flow back for 3 hours with the water bath set as 75 degrees C, when the part was sampled and 1 H-NMR was measured, the proton peak of the acrylic radical origin had disappeared mostly. Then, water bath temperature was lowered to 60 degrees C, the mixed solution (MOI:118g and ethyl-acetate:120g) was added, and 2-ethylhexanoic acid tin:0.6g was added after further 10 - 30 minutes. Heating churning was continued for 3 to 4 hours, and the time of the NCO radical characteristic absorption (2270cm-1) of IR chart disappearing was made into the reaction terminal point. Furthermore, vinyl group content DIN DORIMA made into the purpose was obtained by carrying out desolventization of the ethyl acetate used as a reaction solvent by the evaporator. 1 H-NMR chart of obtained vinyl group content DIN DORIMA was shown in drawing 3, and the attribution was shown in the following figure. Moreover, the physical-properties value was shown in Table 1.

[0061]

[Formula 8]

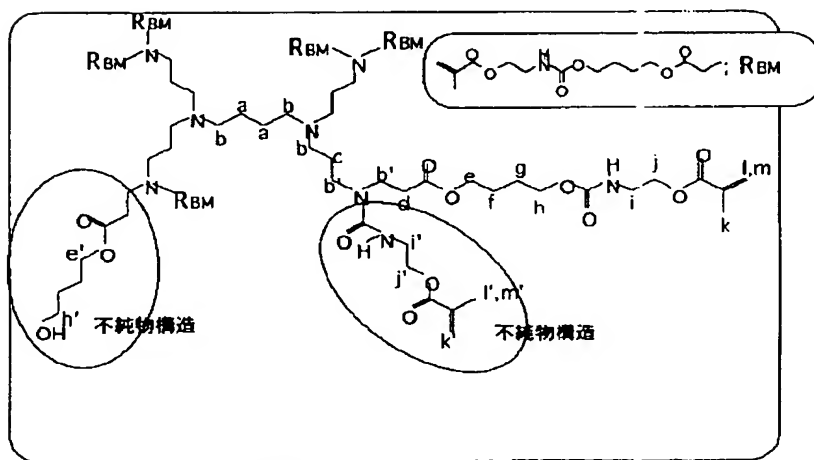
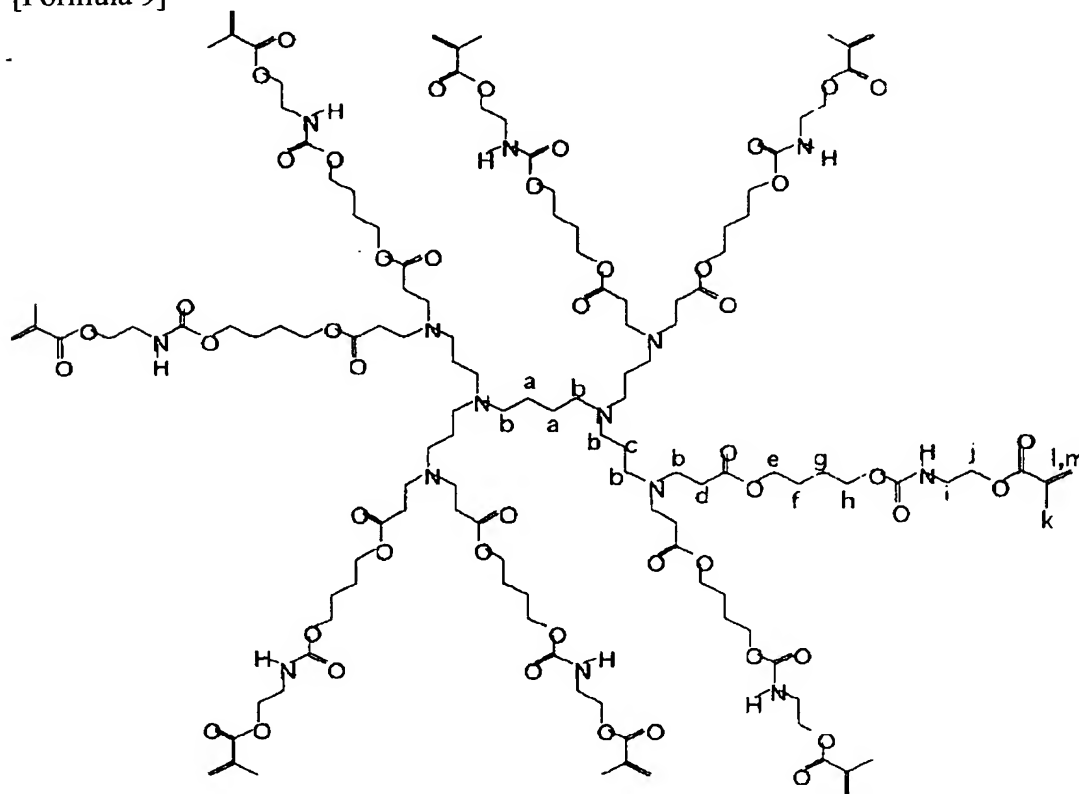


[0062] (Example 2) 4:31.6 g DAB, 4HBA:115g, ethyl-acetate:63g, and methanol:30g were blended with the 500ml 4 opening round bottom flask equipped with churning equipment, nitrogen installation tubing, the thermo sensor, and the capacitor, and after making it flow back for 3 hours with the water bath set as 75 degrees C, when the part was sampled and 1 H-NMR was measured, the proton peak of the acrylic radical origin had disappeared mostly. then, between a reactor and capacitors -- splitting tubing -- setting -- a 80-degree C water bath -- ordinary pressure -- warming -- continuing - churning, vacuum Rhine was further connected from the capacitor upper part, and when ethyl acetate and a methanol were completely distilled off by decompressing to 40 or less mmHg with the water bath which distilled off the solvent and which was lowered to 70 degrees C, viscous liquefied resin was obtained (98% of yield). Then, with a water bath temperature of 70 degrees C as, MOI:115g and ethyl-acetate:260g were added, and also 2-ethylhexanoic acid tin:0.6g was added after 10 minutes. Heating churning was continued for 3 hours and the time of the NCO radical characteristic absorption (2270cm-1) of IR chart disappearing was made into the reaction terminal point. Furthermore, vinyl group

content DIN DORIMA made into the purpose was obtained by carrying out desolventization of the ethyl acetate used as a reaction solvent by the evaporator. 1 H-NMR chart of obtained vinyl group content DIN DORIMA was shown in drawing 4, and the attribution was shown in the following figure. Moreover, the physical-properties value was shown in Table 1.

[0063]

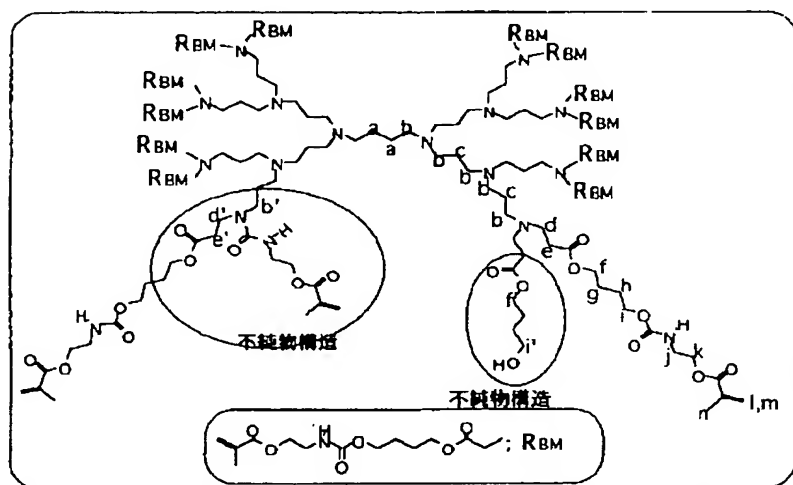
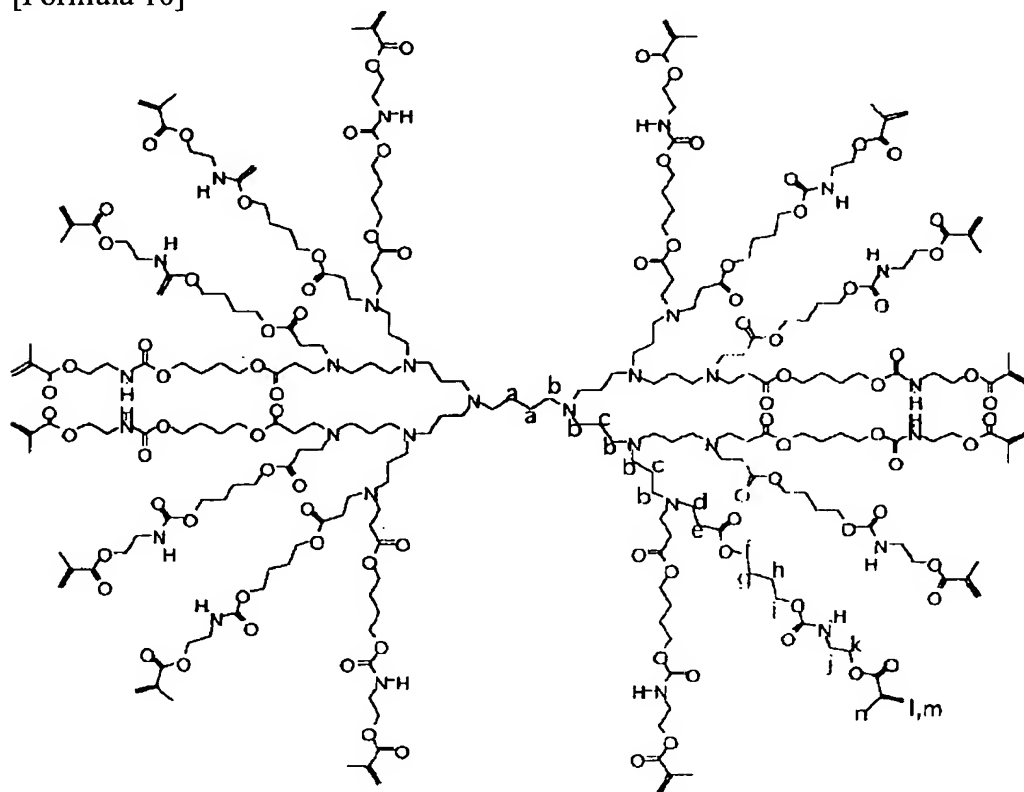
[Formula 9]



[0064] (Example 3) 8:36.65 g DAB, 4HBA:115g, ethyl-acetate:65g, and methanol:30g were blended with the 500ml 4 opening round bottom flask equipped with churning equipment, nitrogen installation tubing, the thermo sensor, and the capacitor, and after making it flow back for 3 hours with the water bath set as 75 degrees C, when the part was sampled and 1 H-NMR was measured, the proton peak of the acrylic radical origin had disappeared mostly. then, between a reactor and capacitors -- splitting tubing -- setting -- a 80-degree C water bath -- ordinary pressure -- warming -- continuing - churning, vacuum Rhine was further connected from the capacitor upper part, and when ethyl acetate and a methanol were completely distilled off by decompressing to 40 or less mmHg with the water bath which distilled off the solvent and which was lowered to 70 degrees C, viscous liquefied resin was obtained (97% of yield). Then, with a water bath temperature of 70 degrees C as, MOI:114g and ethyl-acetate:265g are added, and also 2-ethylhexanoic acid tin:0.6g is added after 10 minutes.

[0065]

[Formula 10]

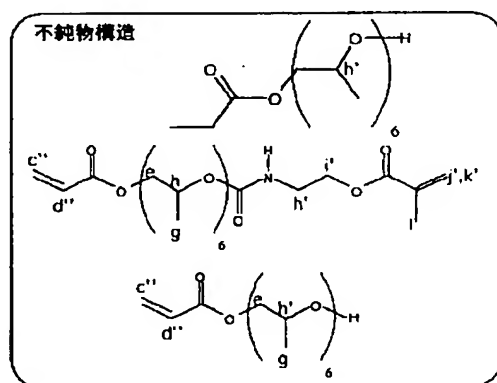
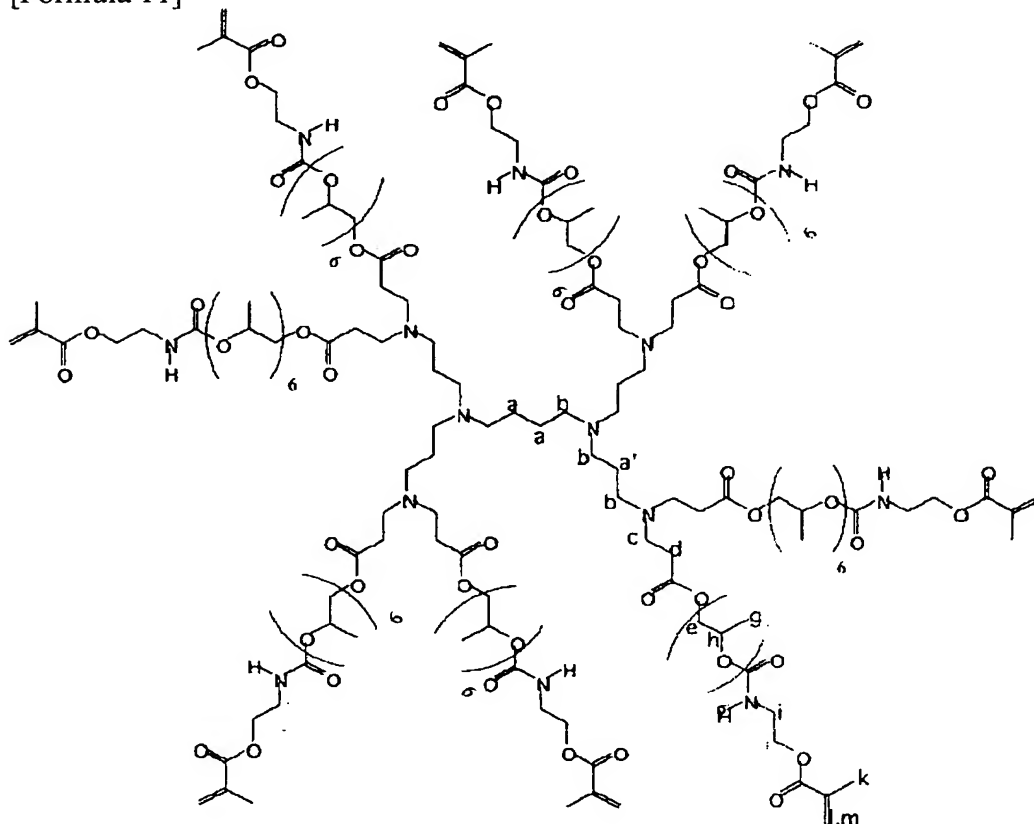


http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web/cgi_ejie

MOI:115g and ethyl-acetate:530g were added, and also 2-ethylhexanoic acid tin:0.6g was added after 10 minutes. Heating churning was continued for 3 hours and the time of the NCO radical characteristic absorption (2270cm^{-1}) of IR chart disappearing was made into the reaction terminal point. Furthermore, vinyl group content DIN DORIMA made into the purpose was obtained by carrying out desolventization of the ethyl acetate used as a reaction solvent by the evaporator. $^1\text{H-NMR}$ chart of obtained vinyl group content DIN DORIMA was shown in drawing 6, and the attribution was shown in the following figure. Moreover, the physical-properties value was shown in Table 1.

[0067]

[Formula 11]

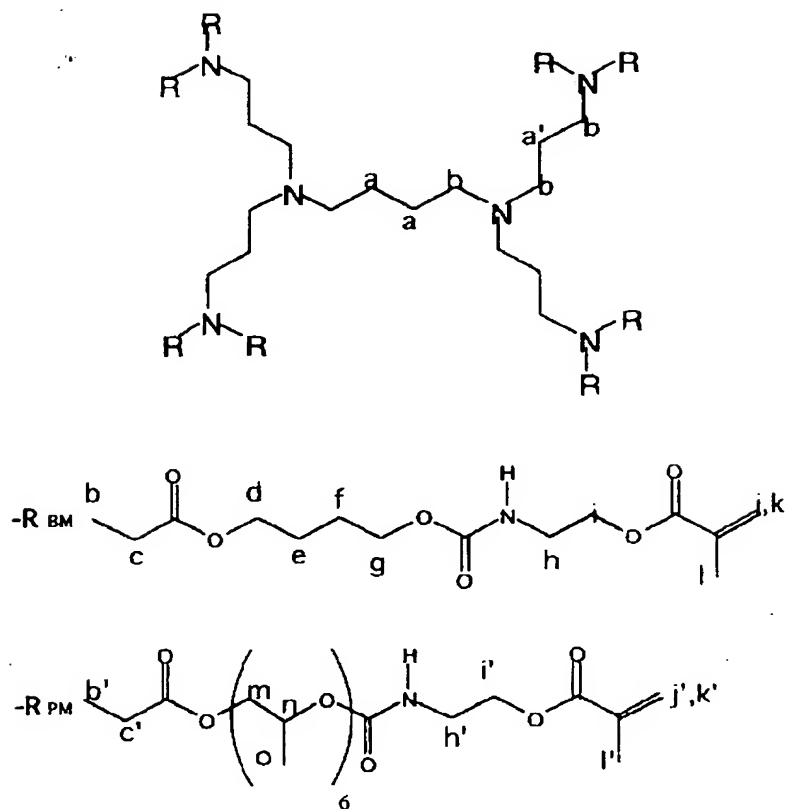


[0068] To the 500ml 4 opening round bottom flask equipped with churning equipment, nitrogen installation tubing, the thermo sensor, and the capacitor, 4:31.6 g DAB, (Example 5) 4HBA: 57.5g, PPG6A:191g, ethyl-acetate:120g, a methanol: 30g was blended, and after making it flow back for 4 hours with the water bath set as 75 degrees C, when the part was sampled and $^1\text{H-NMR}$ was measured, the proton peak of the acrylic radical origin had disappeared mostly. then, between a reactor and capacitors -- splitting tubing -- setting -- a 80-degree C water bath -- ordinary pressure -- warming -- continuing - churning, vacuum Rhine was further connected from the capacitor upper part, and when ethyl acetate and a methanol were completely distilled off by decompressing to 40 or less mmHg with the water bath which distilled off the solvent and which was lowered

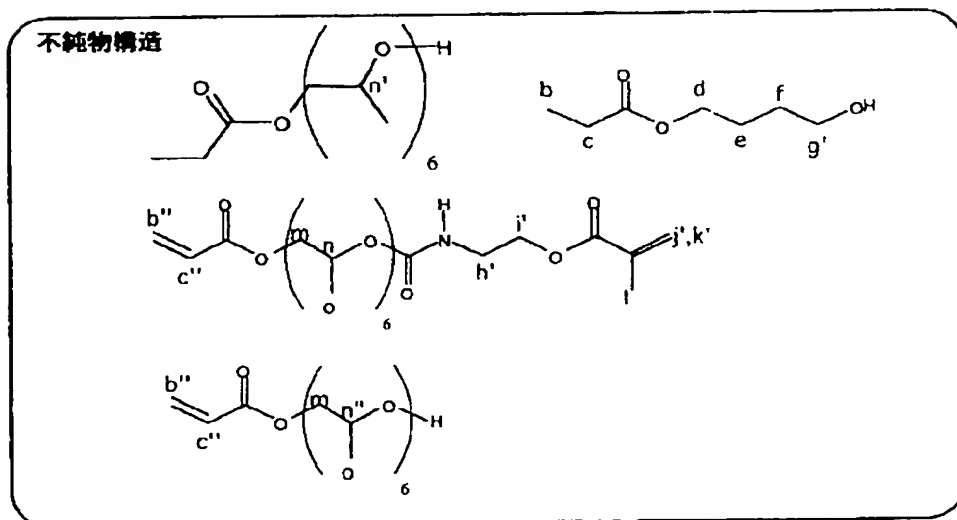
to 70 degrees C, viscous liquefied resin was obtained (98% of yield). Then, with a water bath temperature of 70 degrees C as, MOI:115g and ethyl-acetate:395g were added, and also 2-ethylhexanoic acid tin:0.6g was added after 10 minutes. Heating churning was continued for 3 hours and the time of the NCO radical characteristic absorption (2270cm⁻¹) of IR chart disappearing was made into the reaction terminal point. Furthermore, vinyl group content DIN DORIMA made into the purpose was obtained by carrying out desolventization of the ethyl acetate used as a reaction solvent by the evaporator. 1 H-NMR chart of obtained vinyl group content DIN DORIMA was shown in drawing 7, and the attribution was shown in the following figure. Moreover, the physical-properties value was shown in Table 1.

[0069]

[Formula 12]



(ここで、-Rは -R_{BM} または -R_{PM} であり、-R_{BM} : -R_{PM} = 1:1 (mol ratio)である)



[0070] (Examples 6-23) The ethyl acetate of the multifunctional compound (a) and this which were shown in churning equipment, nitrogen installation tubing, the thermo sensor, the dropping funnel, and the 4 opening round bottom flask equipped with the capacitor all over Table 1, and the equivalent was prepared, and the solution which diluted the active hydrogen content acrylic compound (b) so that it might become 75% of the weight with ethyl acetate was taught to the dropping funnel. The active hydrogen content acrylic compound (b) taught to the dropping funnel was dropped agitating the inside of a flask. Except when HEA was used as an active hydrogen content acrylic compound (b), the multifunctional compound (a) and the methanol of the number of the said mols were further added in the flask (system of reaction). After being immersed in the water

bath set as 75 degrees C and making the system of reaction flow back for 4 hours, the part was sampled, 1 H-NMR was measured and it considered as the terminal point check by disappearance of the proton peak of the acrylic radical origin. then, between a reactor and capacitors -- splitting tubing -- setting -- a 80-degree C water bath -- ordinary pressure -- warming -- the solvent was distilled off, continuing - churning. Furthermore, vacuum Rhine was connected from the capacitor upper part, and when ethyl acetate and a methanol were completely distilled off by decompressing to 40 or less mmHg with the water bath lowered to 70 degrees C, the viscous liquefied object (denatured multifunctional compound (a)) was obtained. Furthermore, water bath temperature was lowered to 60 degrees C, ethyl acetate was newly added so that it might become NV50%, the isocyanate radical content vinyl compound (c-1) was added so that it might become amounts [stoichiometric / which the denatured multifunctional compound (a) contains / active hydrogen, stoichiometric, etc.], and it diluted with ethyl acetate so that the concentration of the whole system of reaction might become 50% further. further -- after 10 minutes and 2-ethylhexanoic acid tin -- 0.5% of the weight of an isocyanate radical content vinyl compound (c-1) -- having added . It is heating churning I then continuously [for 3 hours or more]. The time of the NCO radical characteristic absorption (2270cm⁻¹) of R chart disappearing was made into the reaction terminal point. Furthermore, vinyl group content DIN DORIMA made into the purpose was obtained by carrying out desolventization of the ethyl acetate used as a reaction solvent by the evaporator. The raw material presentation at the time of the obtained vinyl group content DIN DORIMA composition and the property of obtained vinyl group content DIN DORIMA are combined, and are shown in Table 1. Moreover, the physical-properties evaluation result of the dipentaerythritol hexaacrylate (DHPA) of marketing measured by the approach same as examples 1-3 of a comparison and an ethyleneoxide denaturation pentaerythritol thoria chestnut rate (TMPT3EO, TMPT6EO) is also shown collectively.

[0071]

[Table 1]

	原料組成(a)/(b)/(c-1) (モル比)	官能 基数	純度 (%)	平均分子量 (Mn)	粘度(30℃) (cps)
実施例1	DAB4/HEA/MOI=1/8/8	8	93	2331	4360
実施例2	DAB4/4HBA/MOI=1/8/8	8	89	2446	4440
実施例3	DAB8/4HBA/MOI=1/16/16	16	78	4047	7600
実施例4	DAB4/PPG6A/MOI=1/8/8	8	70	4146	620
実施例5	DAB4/(4HBA/PPG6A)/MOI=1/(4/4)/8	8	75	3206	1320
実施例6	DAB8/PPG6A/MOI=1/16/16	16	66	7760	1830
実施例7	DAB4/PEG7A/MOI=1/8/8	8	68	3747	780
実施例8	DAB4/PCL2A/MOI=1/8/8	8	70	3167	7200
実施例9	DAB8/PCL2A/MOI=1/16/16	16	65	5868	6500
実施例10	DAB8/4HBA/(TMI/MOI)=1/16/(8/8)	16	79	4747	6820
実施例11	DAB4/HEA/(合成例4)=1/8/8	8	90	3599	6230
実施例12	DAB4/4HBA/(合成例4)=1/8/8	8	80	3436	5920
実施例13	DAB4/PPG6A/(合成例4)=1/8/8	8	73	5412	1520
実施例14	DAB4/(PPG6A/HEA)/(合成例4)=1/(4/4)/8	8	78	4496	4320
実施例15	DAB4/(PPG6A/4HBA)/(合成例4)=1/(2/6)/8	8	68	3607	3960
実施例16	DAB4/4HBA/(合成例5)=1/8/8	8	69	2715	4750
実施例17	DAB4/HEA/(合成例6)=1/8/8	8	86	3277	3970
実施例18	DAB4/PPG6A/(合成例1)=1/8/8	8	67	4923	3260
実施例19	DAB4/PCL2A/(合成例2)=1/8/8	8	65	4146	7930
実施例20	DAB4/PPG6A/(合成例3)=1/8/8	8	63	4527	6890
実施例21	DAB8/HEA/(合成例6)=1/16/16	16	86	6614	6880
実施例22	DAB8/PCL2A/(合成例4)=1/16/16	16	74	8824	9650
実施例23	DAB8/4HBA/(合成例4)=1/16/16	16	80	6268	1030
比較例1	DHPA	6		550	5900
比較例2	TMPT3EO	3		430	60
比較例3	TMPT6EO	3		560	75

[0072] (Examples 24-47, examples 4-6 of a comparison) Vinyl group content DIN DORIMA obtained in the examples 1-42 was applied by the bar coating machine of #6 on four kinds of films (size -> thickness of the base material for evaluation; 20 micrometers, width-of-face;5cm, die-length;20cm), and the electron ray was irradiated by various DOSE(s) (5, 20, 40kGy). The hardening property of the paint film obtained by the class and electron beam irradiation of vinyl group content DIN DORIMA used for Table 2 (it x-:-tuck[a finger touch trial, ->]-**) Although it is nothing [tuck], it gets damaged by the pawl, and it is based on ** and O:tuck anonychosis and gets damaged. ** : Nothing, A base material adhesive property (rate of paint film un-exfoliating by the Scotch tape friction test), and solvent resistance (survival rate searched for from the weight change before and behind 50 MEK rubbing trials), curl nature (the organoleptics of base material film

transformation nature -- evaluation -> -- nothing [O:curl], extent in which **:edge curves, and x:film will wind), and a wear-resistant evaluation result are shown. Moreover, the evaluation result of commercial dipentaerythritol hexaacrylate and an ethyleneoxide denaturation pentaerythritol thoria chestnut rate (TMPT3EO, TMPT6EO) is also collectively shown as examples 4-6 of a comparison all over Table 2.

[0073]

[Table 2]

	硬化条件 ビニル基含有デンドリマー 原料組成(a)/(b)/(c-1) (モル比)	硬化物性				硬化性				基材接着性				耐溶 剤性 (%)	加工 性	耐磨 耗性	
		電子線加速電圧 60kV		200kV		200kV, 20kGy				200kV, 20kGy							
		(kGy)	(kGy)	(kGy)	(kGy)	PE	OPP	NY	PET	PE	OPP	NY	PET				
		5	20	5	20												
実施例24	DAB4/HEA/MOI=1/8/8	○	○	○	○	○	○	○	○	PE	○	○	△	○	100	○	○
実施例25	DAB4/4HBA/MOI=1/8/8	○	○	○	○	○	○	○	○	○	○	○	○	○	100	○	○
実施例26	DAB8/4HBA/MOI=1/16/16	○	○	○	○	○	○	○	○	○	○	○	○	○	100	○	○
実施例27	DAB4/PPG6A/MOI=1/8/8	△	○	△	○	○	○	○	○	○	○	○	△	96	○	△	
実施例28	DAB4/(4HBA/PPG6A)/MOI=1/(4/4)/8	○	○	△	○	○	○	○	○	○	○	○	○	97	○	○	
実施例29	DAB8/PPG6A/MOI=1/16/16	○	○	△	○	○	○	○	○	○	○	△	97	○	△		
実施例30	DAB4/PEG7A/MOI=1/8/8	○	○	△	○	○	○	○	○	○	○	○	○	97	○	△	
実施例31	DAB4/PCL2A/MOI=1/8/8/8	○	○	○	○	○	○	○	○	○	○	○	○	98	○	○	
実施例32	DAB8/PCL2A/MOI=1/16/16	○	○	○	○	○	○	○	○	○	○	○	○	98	○	○	
実施例33	DAB8/4HBA/(TMI/MOI)=1/16/(8/8)	○	○	△	○	○	○	○	○	○	○	△	90	○	△		
実施例34	DAB4/HEA/(合成例4)=1/8/8	○	○	○	○	○	○	○	○	○	○	△	○	100	○	○	
実施例35	DAB4/4HBA/(合成例4)=1/8/8	○	○	○	○	○	○	○	○	○	○	△	○	100	○	○	
実施例36	DAB4/PPG6A/(合成例4)=1/8/8	○	○	○	○	○	○	○	○	○	○	○	○	98	○	△	
実施例37	DAB4/(PPG6A/HEA)/(合成例4)=1/(4/4)/8	○	○	○	○	○	○	○	○	○	○	○	○	98	○	△	
実施例38	DAB4/(PPG6A/4HBA)/(合成例4)=1/(2/6)/8	○	○	○	○	○	○	○	○	○	○	○	○	97	○	○	
実施例39	DAB4/4HBA/(合成例5)=1/8/8	○	○	○	○	○	○	○	○	○	○	○	○	100	○	○	
実施例40	DAB4/HEA/(合成例6)=1/8/8	○	○	○	○	○	○	○	○	○	○	○	○	100	○	○	
実施例41	DAB4/PPG6A/(合成例1)=1/8/8	○	○	○	○	○	○	○	○	○	○	○	○	97	○	△	
実施例42	DAB4/PCL2A/(合成例2)=1/8/8	○	○	○	○	○	○	○	○	○	○	○	○	98	○	○	
実施例43	DAB4/PPG6A/(合成例3)=1/8/8	○	○	○	○	○	○	○	○	○	○	○	○	95	○	△	
実施例44	DAB8/HEA/(合成例5)=1/16/16	○	○	○	○	○	○	○	○	○	○	○	○	99	○	○	
実施例45	DAB8/PCL2A/(合成例4)=1/16/16	○	○	○	○	○	○	○	○	○	○	○	○	97	○	○	
実施例46	DAB8/4HBA/(合成例4)=1/16/16	○	○	○	○	○	○	○	○	○	○	△	○	100	○	○	
比較例4	DPHA	○	○	○	○	○	○	△	x	x	x	x	x	100	x	○	
比較例5	TMPT3EO	○	○	○	○	x	○	x	x	x	○	○	○	100	x	○	
比較例6	TMPT6EO	○	○	○	○	x	x	x	x	x	○	○	○	98	△	△	

[0074]

[Effect of the Invention] By using the polyfunctional liquefied resin which is hypoviscosity though it is the amount of macromolecules as hardenability resin of a non-solvent mold by this invention It contributes to an improvement of work environment by cheating out of the rate of combination of the safety currently used for the hardenability resin constituent of the usual non-solvent mold, or the low molecular weight compound which has a problem in physical properties as reduction or non-**. And the coating approaches used conventionally, such as a roll coater and a knife coating machine, Film formation can be carried out in printing methods, such as offset printing, gravure, Toppan Printing, and screen-stencil. It can harden by a certain trigger from the former, such as heating, ultraviolet rays, infrared radiation, an electron ray, and gamma irradiation, and the many branch compound which can be stiffened without using a catalyst and an initiator especially in the case of an electron ray, gamma irradiation, etc. is offered.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The model Fig. of DIN DORIMA

[Drawing 2] The model Fig. of DIN DORIMA

[Drawing 3] 1 H-NMR chart of vinyl group content DIN DORIMA obtained in the example 1

[Drawing 4] 1 H-NMR chart of vinyl group content DIN DORIMA obtained in the example 2

[Drawing 5] 1 H-NMR chart of vinyl group content DIN DORIMA obtained in the example 3

[Drawing 6] 1 H-NMR chart of vinyl group content DIN DORIMA obtained in the example 4

[Drawing 7] 1 H-NMR chart of vinyl group content DIN DORIMA obtained in the example 5

[Translation done.]

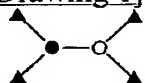
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DRAWINGS

[Drawing 1]



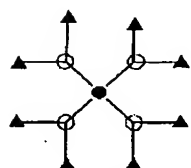
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分岐部位数 ; 1個

枝部位数 ; 5個

末端部位数 ; 4個



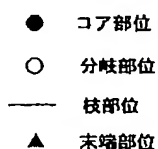
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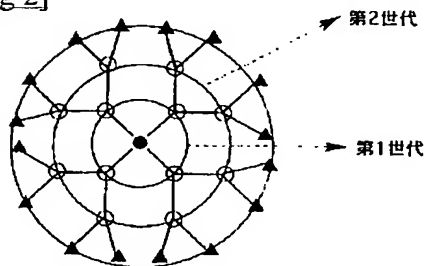
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枝部位数 ; 12個

末端部位数 ; 8個



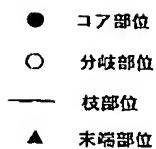
[Drawing 2]



<第3世代デンドリマー>

第2世代

第1世代



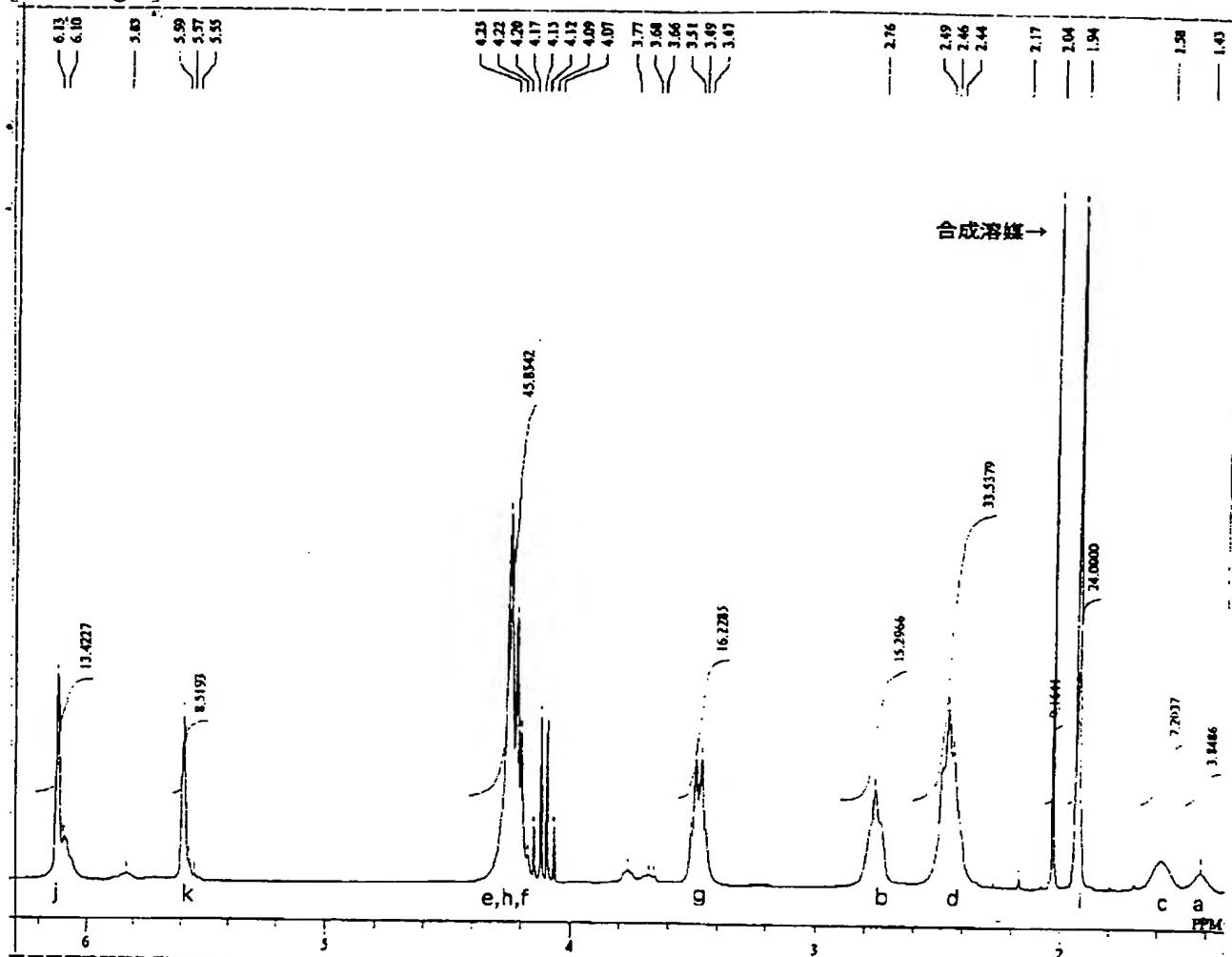
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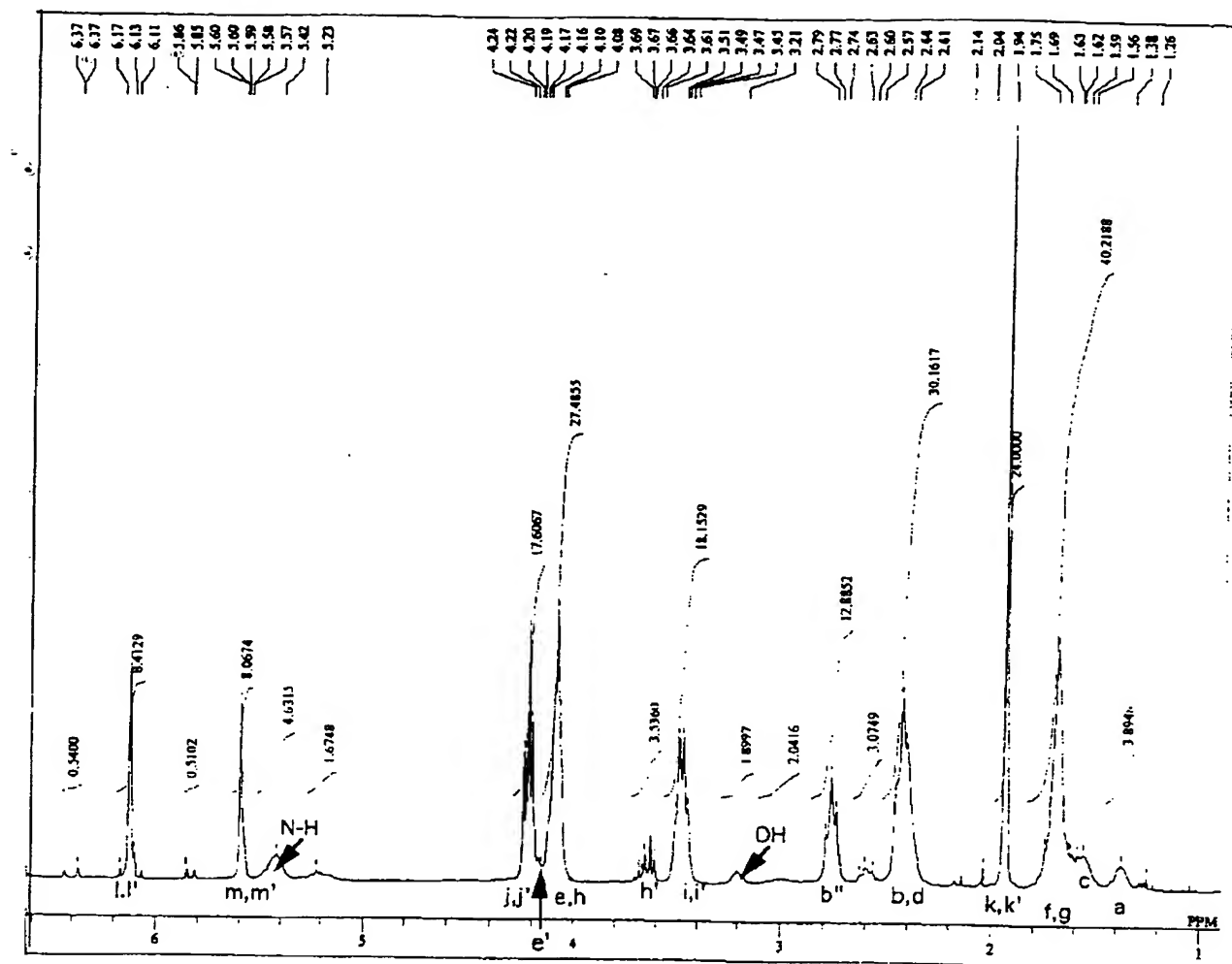
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末端部位数 ; 16個

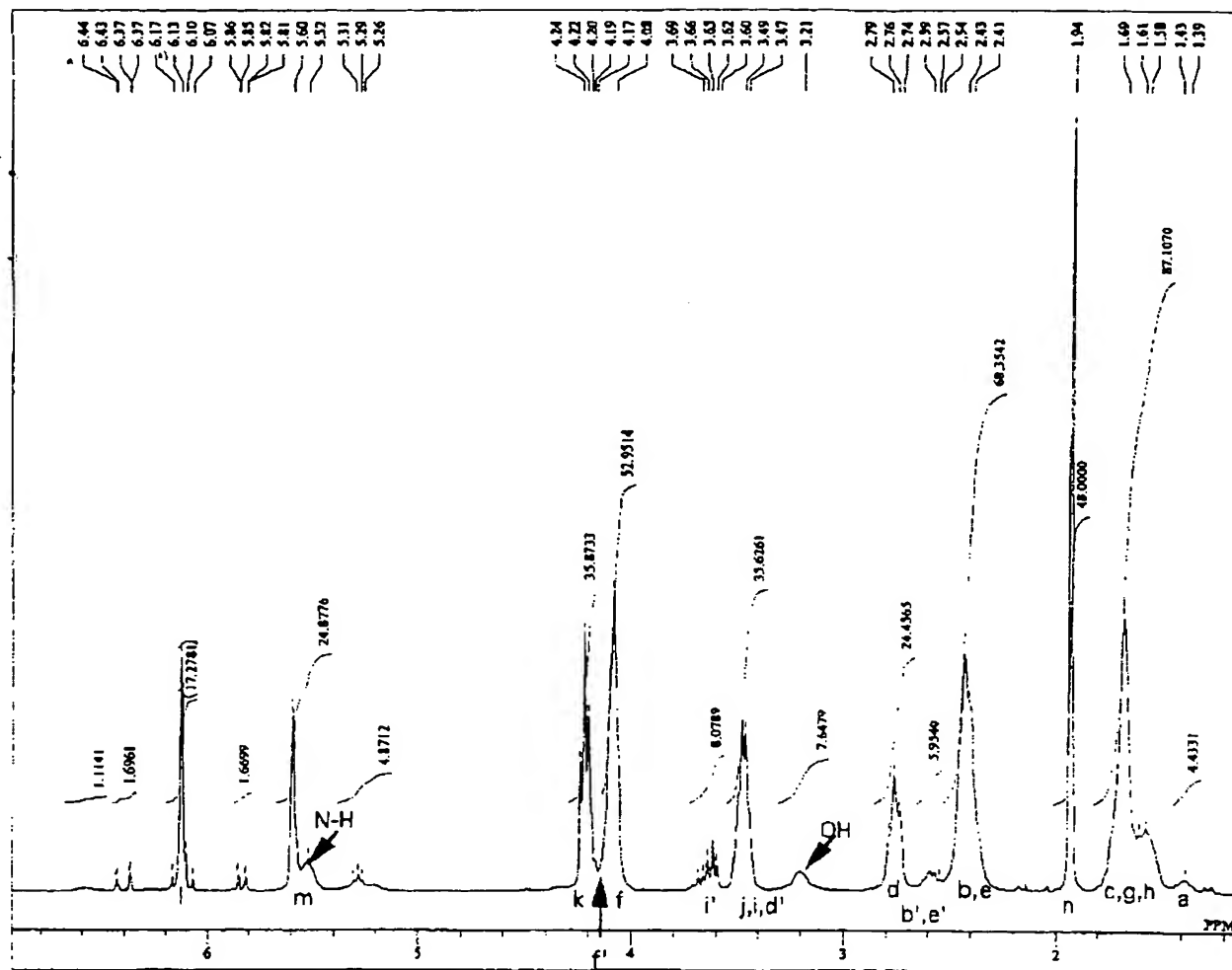
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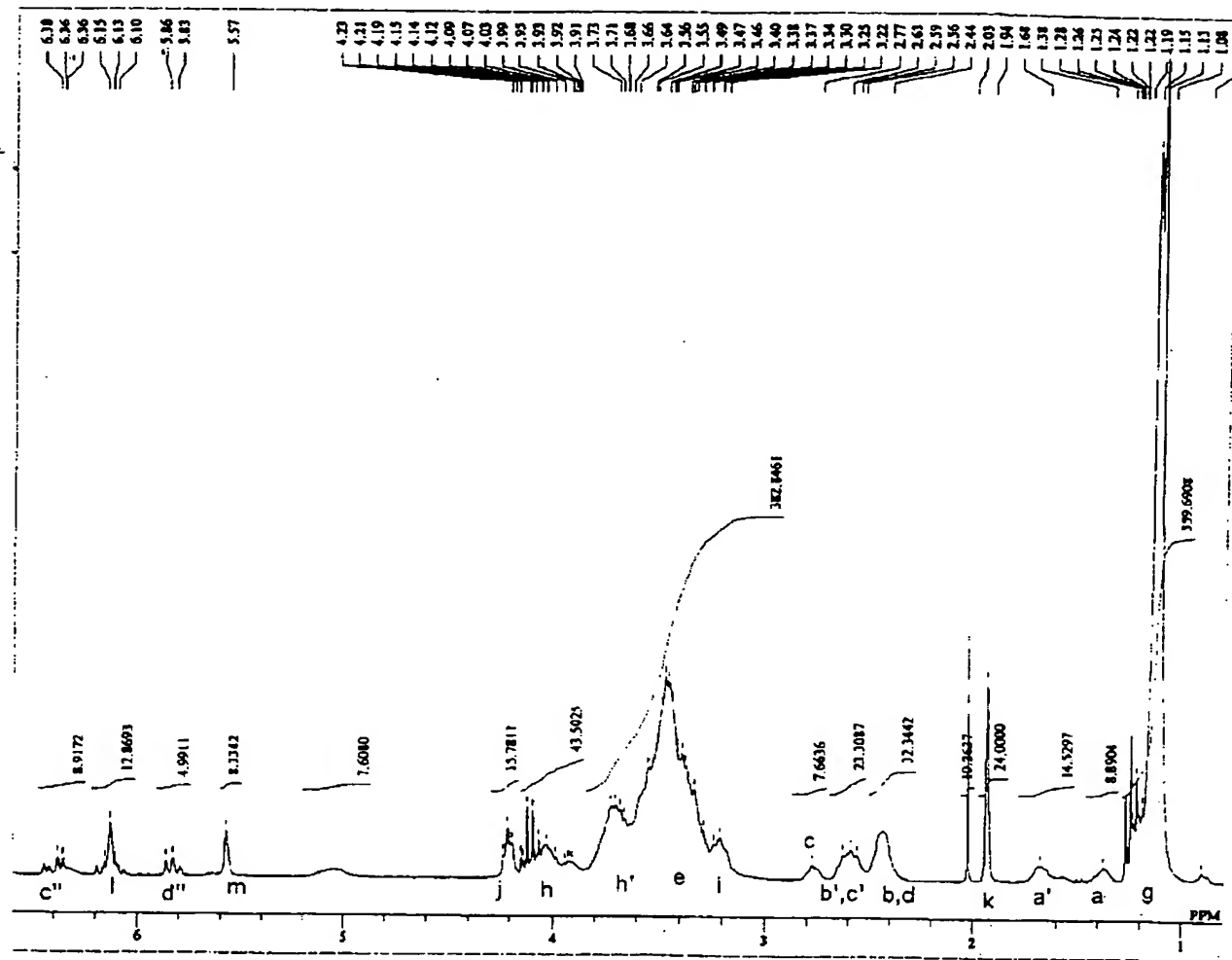
[Drawing 4]



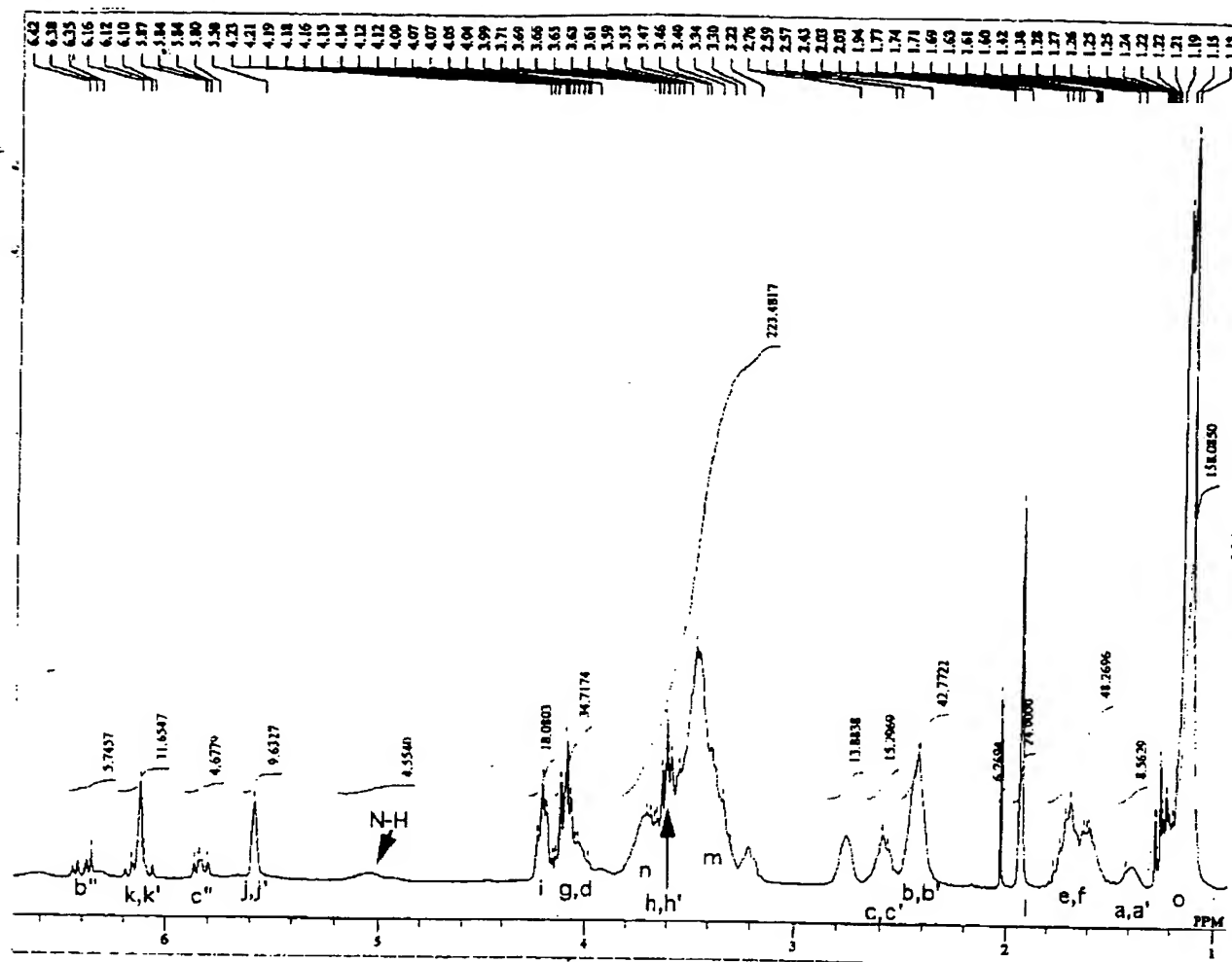
[Drawing 5]



[Drawing 6]



[Drawing 7]



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